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CHELATION BY ORGANIC SUBSTANCES – A FACTOR IN PHOSPHATE AVAILABILITY*

By

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The benefical effect of organic matter on phosphate availability in acid soils is well established, but because of its complexity, it is difficult to determine its specific effect. The benefical effect has been attributed to (1) the protective action of organic colloids, (2) the formation of hydrogen ion from carbonic acid, (3) the formation of organic phosphates that are not highly fixed by soils, and (4) the mineralization, by bacteria, of organic matter containing phosphates.

Certain organic substances, however, react chemically to liberate phosphorus from relatively insoluble compounds. In this reaction, phosphorus becomes soluble because of the formation of stable organo-metallic chelates of iron, aluminum, and calcium. In this paper substantiating data are presented to explain the chemistry of this process and to present observations of plant responses that verify the chemical explanation.

CHEMICAL ASPECTS OF PHOSPHATE AVAILABILITY

Stoichiometric Chemical Precipitation of Iron cr Aluminium Phosphates. Gaarder[10] has reported that maximum precipitation of phosphate by iron and aluminium occurred at pHs of 2 and 4, respectively. Swenson, Cole, and Sieling[25] and

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Struthers and Sieling[24] have demonstrated that with equivalent quantities the isoelectric point of $H_2PO_4^-$ and Fe^{+3} occurs at pH 2·5 to 3·0 and with Al^{+3} at pH 3·5 to 4·0. Swenson et al.[25] found that 3·0 milli-equivalents of NaOH were required to precipitate 3·0 milliequivalents of ferric chloride or of aluminium chloride from the solution; however, when another ion that formed an insoluble precipitate with iron or aluminium was introduced, less NaOH was required for precipitation. They theorized that if one millimole of $H_2PO_4^-$ were added to 3 milliequivalents of Fe^{+3} and if the $H_2PO_4^-$ occupied one of the coordination positions of the iron, then only 2 milliequivalents of NaOH, or enough to fill the two remaining coordination positions, would be required to reach the equivalence point. If the compound $FePO_4$ were formed, no NaOH would be required to induce precipitation. If, on the other hand, HPO_4^{-2} precipitated with Fe^{+3}, one of the coordination positions would be unoccupied, and 1 milliequivalent of OH^- would be required to induce precipitation. Their data indicated that when 2 milliequivalents of OH^- were added in the presence of one millimole of $H_2PO_4^-$, 3 milliequivalents of Fe^{+3} or Al^{+3} were precipitated. Further, when more than one millimole of $H_2PO_4^-$ was added to 3 milliequivalents of Fe^{+3}, 2 milliequivalents of OH^- were required to reach the equivalence point.

These results indicate the formation of basic iron and aluminium phosphates, $Fe(H_2O)_3(OH)_2H_2PO_4$ (strengite) and $Al(H_2O)_3(OH)_2H_2PO_4$ (variscite), in which $H_2PO_4^-$ occupied only one of the coordination positions of hexahydrated iron or aluminium ions. By means of X-ray and electron microscope technics Cole and Jackson[5] identified these compounds of iron and aluminium phosphates as strengite and variscite.

Effect of pH on formation of basic iron and aluminium phosphates. Many investigators have observed that phosphate precipitation by iron or aluminium in solution and phosphate fixation in soil increases as the pH of the solution or soil decreases. Swenson et al.[25] and Struthers and Sieling[24] have pointed out (figure 1) that as the pH of the precipitating solution was increased from the isoelectric point, 90% of the phosphate was still combined with iron or aluminium at pH 6·5, and 70% with aluminium at pH 9·0. The addition of lime to change the pH from 5 to 6 releases only 7% of the phosphate chemically combined with iron or aluminium. Although the practice of liming soils to increase their pH value with subsequent release of fixed phosphate is sound, it is of limited value.

Effect of chelating agents on phosphate precipitation by iron and aluminium. Many analytical procedures for determining replaceable phosphate in soils are based on the use of salts of organic anions. The Dyer citric acid method, the Tamm oxalic acid method and the Egner lactic acid method are examples of such procedures. Dean and Rubins[7] have compared the effectiveness of fluoride, citrate, tartrate, arsenate, and acetate for removing adsorbed phosphorus. Kurtz, DeTurk, and Bray[16] found that various anions replaced adsorbed phosphate in the following order: fluoride, oxalate, citrate, bicarbonate, borate, acetate, thiocyanate, sulfate, and chloride.

Sieling and coworkers[3,24,25] have reported the effect of 19 organic anions and 6 sugars in preventing phosphate precipitation by iron and aluminium through the pH range of 3 to 8. They concluded that certain organic substances were effective in preventing phosphate precipitation at the pH values common to agricultural soils, pH 4 to 7. Some were more effective at low pHs; some at the moderately acid range of pH 5 to 6; and others at the neutral point or above. Citrate, the most effective organic anion, completely prevented the precipitation of phosphate by iron and aluminium; however, tartrate and oxalate were effective
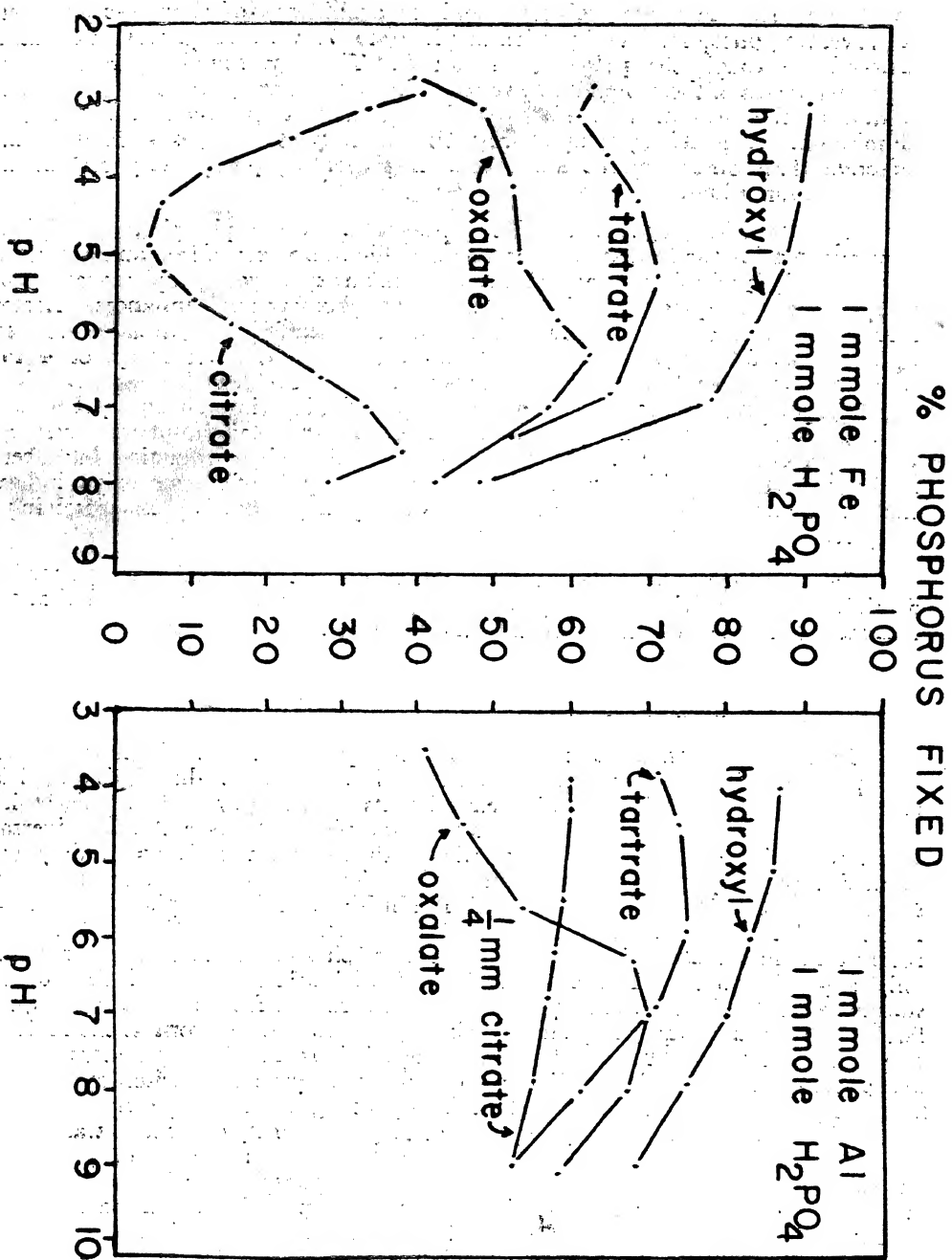
Figure 1. Effect of pH and Organic Anions on Phosphate Precipitation.

also (figure 1). Fructose, galactose, maltose, arabinose, and rhamnose were active in preventing phosphate precipitation at pH 6 to 7, whereas glucose was almost ineffective through the pH range of 3 to 9. These investigators pointed out that the effectiveness of these organic substances in preventing phosphate precipitation is due to the formation of highly stable organometallic complexes of iron and aluminium. Aliphatic hydroxyorganic acids and aromatic hydroxyacids were more effective than other organic substances in preventing phosphate precipitation by iron and aluminium.

Effect of chelating agents in solubilizing phosphates. Since phosphate precipitation is prevented by the formation of organo-metallic complexes of iron and aluminium, the relatively insoluble iron and aluminium dihydroxy dihydrogen phosphates should be solubilized in aqueous solutions by these complex-forming substances. Leclerc[17] found that 10% of the phosphate from variscite and 3% from strengite were solubilized by 2·5 millimolar citrate solutions through the pH range of 4 to 7. Angelini[1] observed that dilute solutions of the calcium chelating agents (citrate, oxalate, and ethylenediamine tetraacetate) were effective through the pH range 4 to 7 in solubilizing rock phosphate. At pH 7·0 the total phosphorus in solution was 2·4% for oxalate, 9·0% for citrate, and 89·6% for ethylenediamine tetraacetate. Additional studies with nine rock phosphate samples of diverse origin indicated that the ethylenediamine tetraacetate was equally effective in dissolving all samples.

Johnston[13,14,15] has studied the action of many organic compounds on dicalcium and tricalcium phosphate and reported that the a-hydroxy aliphatic and aromatic acids were the most effective in dissolving these substances.

BIOLOGICAL ASPECTS OF PHOSPHATE AVAILABILITY

Effect of organic substances on phosphate uptake by plants. Although manure has a low phosphorus content, many investigators have reported that it is an efficient source of phosphate. The extensive experiments of Midgley and Dunklee[20] have indicated that plant responses to manure and phosphate were almost universally better when the two materials were applied at the same time than when they were applied separately. In studies of the utilization of phosphorus from manure and superphosphate, McAuliffe, Peech and Bradfield[19] found that phosphorus fertilization had little effect on the yield of rye grass, although the plants that had received manure contained a higher percentage of phosphorus than those receiving only superphosphate. Dalton, Russell, and Sieling[6] have reported that organic substances containing almost no phosphate had the same effect as soluble phosphate fertilizer in increasing phosphate uptake by plants. Using corn as the indicator crop in the greenhouse, 80 pounds of P_2O_5 applied as KH_2PO_4 per acre gave a phosphorus uptake of 70 milligrams to a pot, whereas a comparison treatment of 2 tons of glucose per acre without soluble phosphate gave a phosphorus uptake of 63 milligrams. When rock phosphate at 80 pounds of P_2O_5 per acre was applied in the same experiment, the plant material contained 58 milligrams of phosphorus for each pot. The combination treatment of rock phosphate and 2 tons of glucose produced plant material containing 78 milligrams of phosphorus for each pot, an increase in phosphorus uptake of 35%. Sucrose, starch, and pectin were applied in additional treatments with similar phosphorus responses. The effect of organic matter in making phosphate available was even more outstanding in an experiment where ladino clover was grown for 42 weeks. Dalton *et al.* suggested that the effect of the organic substances on phosphorus uptake was due to the formation, by soil

micoorganisms, of citric, oxalic, tartaric, or other organic acids capable of chelation with iron, aluminium, and calcium, thereby minimizing the precipitation of phosphate or actually solubilizing some soil phosphate. Results by Warder[29] indicate that a mulch treatment increased the penetration of readily available phosphate in a three-year period. Eggart, Kardos, and Smith[8] found that a surface application of superphosphate was more effective in supplying P_2O_5 on a mulched area than on a sod cover area.

In a 3×3 factorial greenhouse experiment with Merrimac fine sandy loam (pH 6·3), wheat was grown using three application rates of P_2O_5 as superphosphate (0, 60, and 120 pounds per acre) and three rates of oxalic acid (0, 240, and 480 pounds per acre). The relative dry matter yields for the three applications of P_2O_5 were 100, 124, 148, and the relative amounts of phosphorus taken by the crop were 100, 118, and 153. Oxalic acid alone did not appreciably influence the yield of dry matter or phosphorus uptake. The response from the combination treatments of superphosphate and oxalic acid was a highly significant interaction effect. From the 1 P_2O_5—1 oxalic acid treatment, dry matter yield and phosphorus uptake were 90% of the 2 P_2O_5 treatment; whereas the combination treatment, 1 P_2O_5—2 oxalic acid, resulted in a relative yield of 174 and a phosphorus uptake of 162, or 17% and 7% more than the 2 P_2O_5 treatment. From these data it was concluded that the oxalate anion was highly effective in protecting the applied superphosphate from fixation or in solubilizing additional soil phosphate through the chelation of iron, and aluminium.

A subsequent greenhouse experiment was conducted to measure the availability of radioactive superphosphate (1) as affected by oxalate and sulfate anion applied in a band "separate from" or "combined with" the superphosphate applied in a band.

Three sources of oxalate anion were used : oxalic acid at 310 pounds per acre and equivalent amounts of sodium and ammonium salts. The ammonium oxalate treatment was equal to 75 pounds of nitrogen per acre. Ammonium sulfate was the sulfate source and the 75 pound nitrogen source in the oxalic acid and sodium oxalate treatments. The soil was a Merrimac fine sandy loam of pH 6·3 with 20 pounds of Truog available phosphorus[27] per acre. Two P_2O_5 levels, soil level and 100 pounds of P_2O_5 added as superphosphate, were used. Single cross hybrid corn in three replications was grown for seven weeks.

The dry matter yields and phosphorus uptake (2) listed in table 1 indicate the response of the corn to phosphate fertilization. The oxalic acid treatment on the soil level of phosphorus increased the yield and phosphorus uptake as compared to the ammonium oxalate and sulfate treatments. This response was unexpected, since in the previous experiment with wheat, oxalic acid did not affect the dry matter yield or phosphorus uptake. When the anion materials were separated from superphosphate, they did not change the percentage of phosphorus derived from the applied fertilizer or phosphorus "A" value of the soil[9] (table 2). When the anion materials, however, were combined with the superphosphate, striking differences in phosphorus uptake were found. The ammonium or sulfate ion increased plant phosphorus derived from the fertilizer from 38·0 to 41·6%. Robertson et al.[22] have reported similar results from mixing ammonium sulfate and superphosphate. The effect of the oxalate anion is to increase the availability of soil phosphate as indi-

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1. The tagged superphosphate was supplied by Bureau of Plant Industry, Soils, and Agricultural Engineering, U. S. Department of Agriculture.
2. Chemical analysis by D. J. Albritton.

cated by the phosphorus A values. These data are interpreted to indicate that oxalate has solubilized soil phosphate by the chelation process. It is apparent that in the ammonium oxalate superphosphate combined treatment, ammonium ion increases the uptake of applied fertilizer and oxalate ion increases the availability of soil phosphate. In the sodium oxalate superphosphate treatment, the oxalate ion increases the availability of soil phosphate. In the oxalic acid superphosphate treatment both the oxalate ion and the hydrogen ion increase the availability of soil phosphate. Apparently, the quantity of soil phosphorus solubilized by the oxalate ion is greater than the quantity of soil phosphorus solubilized by the hydrogen ion. Furthermore, the action of oxalate ion in solubilizing soil phosphorus is so great that it overshadows the effect of the ammonium ion on the uptake of applied fertilizer.

Table 1. Dry Matter Yield and Phosphorus Uptake of Corn
(average of three replicates)

Treatment[1]	Dry Matter Yield grams/pot			Phosphorus Uptake milligrams/pot		
	OP[2]	P sep	P com	O P	P sep	Pcom
$(NH_4)_2SO_4$	4·79	7·79	8·16	10·35	10·36	12·44
$(NH_4)_2C_2O_4$	4·40	7·55	5·76	10·13	9·46	9·54
$Na_2C_2O_4$	3·27	7·84	6·31	6·40	11·05	9·73
$H_2C_2O_4$	5·62	8·21	8·01	13·02	11·00	11·96

1. N added to all treatments at 75 pounds/acre.
   Oxalate equivalent to 310 pounds $H_2C_2O_4$/acre.
2. O P—soil phosphate level
   P sep—100 pounds P_2O_5/acre separate from SO_4 or C_2O_4 anion
   P com—100 pounds P_2O_5/acre combined with SO_4 or C_2O_4 anion

Table 2. Phosphorus A Values and Percentage of Phosphorus Derived
from Superphosphate Treatments
(average of three replicates)

Treatment[1]	%Plant P Derived from Fertilizer		Phosphorus A value pounds P_2O_5/acre	
	Separate[2]	Combined[3]	Separate	Combined
$(NH_4)_2SO_4$	38·0	41·6	163	144
$(NH_4)_2C_2O_4$	37·7	29·1	165	243
$Na_2C_2O_4$	38·1	25·8	162	287
$H_2C_2O_4$	37·0	23·8	170	318

1. N added to all treatments at 75 pounds/acre.
   Oxalate equivalent to 310 pounds $H_2C_2O_4$/acre.
2. SO_4 and C_2O_4 anion materials in band separate from banded super.
3. SO_4 and C_2O_4 anion materials combined with banded super.

DISCUSSION

Citrates, oxalates, lactates, tartrates, and other organic anions prevent the precipitation of phosphate by iron and aluminium. These anions are also employed as analytical reagents in determining available phosphate in soils. It is believed that the ability of these anions to extract phosphate from soils is due to the formation of stable organo-metallic chelates of iron, aluminium, and calcium, the mettalic ions that form insoluble phosphates in soils. The phosphorus of variscite, strengite, rock phosphate, and soil phosphate has been solubilized by citrate, oxalate, and ethylenediamine tetraacetate through the pH range of 4 to 7. Ethylenediamine tetraacetate, a synthetic chelating agent, was more effective than the other organic anions at pH 7·0. The amount of soluble phosphate obtained from the phosphate salts of iron, aluminium, and calcium is increased markedly through the inactivation of metallic ions by chelating agents.

One theory of phosphate fixation in that soluble phosphates combine directly with clay minerals. Many investigators have demonstrated, however, that the phosphate fixation ability of clays is greatly reduced by acid extractions to remove aluminium and iron. The presence of large quantities of exchangeable aluminium in electrodialized clay[12,18,21] indicates further the importance of aluminium in the phosphate fixation process. Turner and Rice[6] demonstrated that the fluoride ion formed a complex ion with aluminium, which resulted in the solubilization of aluminium phosphate, whereas iron phosphate was not solubilized. The reliability of Bray's ammonium fluoride method[4] for determining available phosphate in soils indicates that aluminium phosphate is more significant than iron phosphate in fixation.

At any pH value within the entire range of values for agricultural soils some organic anions are markedly effective in preventing precipitation of phosphate by iron and aluminium. These anions solubilize phosphate from variscite, strengite, rock phosphate, and soil phosphate. Schwartz, Varner, and Martin[13] observed that only acetates and formates were produced in incubated soil samples ; however, the effect of organic matter on the availability of the phosphate in superphosphate and rock phosphate has been the subject of numerous investigations. Bauer[2] found increased phosphate uptake where mixtures of organic matter and rock phosphate had been added to soils. Gerretsen[11] found that the action of microorganisms increased the availability of the phosphate in rock phosphate, whereas Waksman[28] reported that the action of certain constituents of humus increased the solubility of rock phosphate.

To the many beneficial effects previously attributed to soil organic matter, we can now add that of making soil phosphorus more available. Practical farmers have long known that as soil organic matter decreased, there was a parallel increase in the requirement of fertilizer phosphate for high crop production. Organic matter from manure, crop residues, previous crop roots, and sloughed root hairs of the growing crop is the source of metabolic products of microbiological decomposition. These metabolic products in small concentration form highly stable organo-metallic complexes with the phosphate coming into solution and being available to plant roots.

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SOME PROBLEMS CONCERNING SOIL ORGANIC PHOSPHORUS

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During the last decades much attention has been paid to the organic bound soil phosphorus. In spite of the fact that at present no quite accurate methods are available for the determination of the total amount of soil organic phosphorus, it is undisputed that this fraction represents a considerable part of the total phosphorus in most soils. Figures ranging from 5 to 95 per cent of total phosphorus, with an average of about 50 per cent, have been found in Finnish soils by the author. The highest amount of organic P, 1950 p. p. m. was analyzed for a peat soil.

The composition of this fraction and its role in plant nutrition are interesting problems which are still open. Some years ago it was generally believed that about one half of soil organic phosphorus occurred in the form of nucleic acids and the other half as phytin or other inositol phosphates. Phytin and lower inositol phosphates have indeed been isolated from soils in quantities often corresponding to about one half of the soil organic phosphorus (BOWER 1945, NORGAARD PEDERSEN 1953 etc.). This, however, is not the case with nucleic acids. Until present, only fairly low amounts of their constituents have been isolated from soils. Hence, in recent papers (ADAMS et al. 1954, Rothamsted Report 1954, p. 51) the conclusion has been drawn that the amount of nucleic acid phosphorus in soils cannot generally be higher than 5 per cent of the total organic phosphorus. This means that a large part of soil phosphorus exists in forms at present unknown.

The fact that phytin and other inositol phosphates are so abundantly found in soils is far more surprising than would have been an accomulation of nucleic acids. Nucleic acids are common constituents of all living organisms and form a large part of the organic phosphorus carried into soil in plant and animal residues and in the cells of microorganisms. But as far as known, phytin is a typical compound of seeds and has not been detected in the vegetative parts of the plants or in microorganisms. In animals it also is unknown except in feces of animals fed by a ration containing grain. Some evidence of the microbial synthesis of phytin in soils has been reported (JACKMAN 1951, SMITH & CLARK 1951), but these results are not yet satisfactorily proved. In every case according to our present knowledge, the amounts of phytin aunually coming to soil cannot be large. Thus the soil phytin must be well protected against the attacks of mineralizing agents and represent the result of a long term accumulation. Also another possibility must be taken into consideration : the organic phosphorus indentified with phytin or lower inositol phosphates may be some other compounds, a supposition corroborated by the findings of SMITH and CLARK (1952).

The importance of soil organic phosphorus in plant nutrition is also an unsolved question. It has been shown that plants are able to take up their phosphorus from pure preparations of phytin, nucleic acids and other organic phosphorus compounds, also without the aid of microorganisms (WEISSFLOG & MENGDEHL 1933 etc.). No experiments, however, have proved that the native soil organic phosphorus as such could be utilized by plants, even the water-soluble part of this

fraction appears to be unavailable (KAILA 1948 etc.). A mineralization process is necessary and on its intensity depends the value of soil organic phosphorus as a source of plant nutrition.

Experiments concerning the mineralization of soil organic phosphorus have been carried out under different conditions. Generally, the increase in soluble inorganic phosphorus has been taken to mean a mobilization of organic bound phosphorus. This evidence, however, is not sufficient to prove that mineralization of organic phosphorus really has occurred, particularly, if liming or other treatments able to change the solubility of soil phosphorus have been used. Only an increase in the amount of inorganic phosphorus equal to the decrease in the organic phosphorus content is a sufficient proof.

In an experiment performed by the author soil samples were incubated for one year at various temperatures and with occasional drying and wetting. The total amounts of inorganic and organic phosphorus extracted by successive treatment with 4 N sulphuric acid and 0·5 N sodium hydroxide from some of the samples were the following : (I=inorganic P p. p. m. O=organic P p. p. m.).

Soil	Silt		Clay loam		Muddy clay		Sand		Sand	
	I	O	I	O	I	O	I	O	I	O
Original	580	370	620	310	630	190	390	540	120	220
Inc. at 7°C	610	340	620	310	650	160	380	540	150	190
,, 20°C	620	340	650	300	630	170	400	520	160	190
,, 35°C	640	350	640	320	650	160	420	500	170	190
,, 50°C	790	340	750	220	690	120	570	400	240	150

These data indicate that the mineralization of organic phosphorus has not been marked except in the samples incubated at 50°C. At this temperature some weathering of mineral material has taken place, since the increase in the soluble inorganic phosphorus is higher than the corresponding decrease in the organic phosphorus content. At the lower temperatures the decrease in the organic phosphorus fraction ranges from 0 to 40 p. p. m. These results are well in accordance with previous observations (KAILA 1948, BOWER 1949). In this connection attention must be paid to the poor accuracy of the methods we have for the determination of total organic phosphorus in soil. Often a difference lower than 20 p. p. m. is not significant. Therefore, too for going conclusions must be avoided.

In experiments of this kind the date obtained represent the net results of microbial synthesis and decomposition. They give no idea of the speed of these contrary proccesses or of the whole phosphorus cycle. Some investigations in which the isotope technique was employed (GORING 1955) indicate that the transformations of phosphorus in soil may be fairly rapid. Perhaps in soils where plant roots adsorb phosphate ions the amount of mobilized organic phosphorus which can be utilized by plants during the growing season is higher than the quantities found to be mineralized in incubation experiments. That soil organic phosphorus may be of significance in the phosphorus nutrition of plants was verified by pot experiments carried out by EID et al. (1954), but this was true only at higher temperatures, in these experiments at 35°C.

Obviously the mineralization of soil organic phosphorus is closely connected with the decomposition of organic matter in general. Thus the mobilization of organic phosphorus brought about by different kind of treatments may lead to undesirable results. In view of the important role soil organic matter plays in the fertility it probably is more profitable to apply fertilizers than to try to mobilize nutrients that are more or less essential constituents of soil organic matter. The problem in the modern agriculture seems to be how to protect soil organic matter and, if possible, enhance it and simultaneously also soil organic phosphorus.

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MECHANISM OF LIME SAVING BY THE APPLICATIONS OF PHOSPHATES

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There is an adage that a lime country is a rich country but of all the constituents none is so seriously liable to loss as lime. Serious losses of lime have been observed by various soil scientists in different parts of the world. Lyon and Bizzell[1] observed an average annual loss of 995 lbs. of $CaCO_3$ per acre from the bare plots while 535 lbs. from plots that grew crops. Robinson[2] reported the annual losses from Rothamsted-soils containing free $CaCO_3$ to be 500 lbs. per acre but in North Wales where soils contain from 0·15 to 0·35 per cent exchangeable lime, the annual loss has been reported to be 100-200 lbs. by Williams[3], the highest losses occurring from soils richest in lime. Russell[4] states that $CaCO^3$ is being washed continually from the Rothamsted soils which contained approximately 5% calcium carbonate in 1843 at an average annual rate equivalent to 2-4 cwts. of $CaCO_3$ per acre depending upon the amount and solubility of $CaCO_3$ in the soil. Davies[5] found that a soil having a lime requirement of 40 cwts. of $CaCO_3$ per acre lost 1 cwt./acre annually if 25 cwts. of $CaCO_3$ were added, 3 cwts/acre if 50 cwts. were given and 6 cwts./acre if 100 cwts. were spread. Tuorila[6] found from the analysis of many Finnish liming experiments that the average annual loss of $CaCO_3$ from acid soils was roughly proportional to the dressings of $CaCO_3$ given. The Gottingen fields[7] in Germany show a maximum loss of 206 lbs. of CaO while the minimum being 175·8 lbs. In Aberdeen[8] only 76 lbs. of CaO were lost from one acre of land. An average of 90 analyses of Illinois well-waters, 3 million pounds of water, *i. e.* the average annual drainage per acre for Illinois contained 330 lbs. calcium. By adding 10 tons of ground lime per acre, the loss during ten years was 780 lbs. per acre. MacIntire and Sterges[9] found that from a soil with pH 6·7—7·4 and receiving an annual average rainfall of 50·8″, 100 lbs. of calcium is lost, whilst by adding 2 tons of $CaCO_3$ per acre the loss is almost fivefold. In Holland,[10] on arable land the average CaO losses in drainage-water amount to 400 Kgm. in clayey soil, 250 Kgms in peaty soils, 200 Kgms. in sandy organic soil and 150 Kgms. in sandy soils per hectare annually. The Illinois station[11] concludes that the equivalent of 540-760 lbs. of $CaCO_3$ is leached away from the surface 21 inches of the soil annually. Important test in the upper Brickfield at Cockle Park (Northumberland County Experiment Station)[12] on the loss of lime from arable land was started in February 1904 when 10 tons of ordinary lime per acre was applied and swedes grown for nine years. The roots removed only 180 lbs. of lime but in June 1913, the top six inches contained only five cwts. $CaCO_3$ equivalent to lime while the second six inches of the soil contained 33 cwts. of lime per acre. It has been found that 1—2 tons of lime applied to soils will produce good results for 8—10 years. The compensation allowed by Hall and Voelcker in England for lime application assumed that the effect of liming would last for 7

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years on grassland and for 5 years on arable land. Voelcker found 0·75 per cent $CaCO_3$ to be a suitable amount in soils but as soon as it reached below 0·5 per cent, the crops became susceptible to various diseases.

The loss of lime has been found to be aggravated by carbonated waters, ammonium salts used as fertilizers and keeping the soil bare. Russell[13] reports that ammonium sulphate removes half its own weight of chalk. Humus[14] has been found to check loss of lime. On an acid silt loam at Cornell Station[15], New York, the soil which was acidic upto 3 feet did not increase the amount of lime found in drainage when 3000 lbs. of burnt lime per acre was applied. The Rothamsted experiments[16] clearly show that the dunged plots lost only 590 lbs. of $CaCO_3$ while complete minerals including ammonium sulphate as fertilizer removed 1010 lbs. per acre. Sodium nitrate was found to decrease the loss, the corresponding loss of $CaCO_3$ being 564 lbs./acre. Growing crops also minimize this loss of lime. Gardner[17] reports that superphosphate, K_2SO_4 and Kainit do not increase the loss to any extent. Organic materials like farm-yard manure tend to decrease the loss of chalk from soils. Basic slag has also a tendency to reduce this loss.

Kelley[18], Puri[19] and others have shown that carbonates of alkali make the soluble calcium insoluble by forming $CaCO_3$ and thus reduce the concentration of calcium ions in the water extracts. Unpublished data of Dhar and Goel shows that citrates and tartrates are good lime saviours. K_2SO_4 has been found by MacIntire and co-workers[20] to save lime.

In an article on "New Aspects of the Value of Phosphates", Dhar[21] stated that calcium phosphate can be very effective in decreasing the acidity of soils and hence can act as a saviour of lime and in the support of this contention, quoted the following results obtained by Burgess.

Treatment	Total crop grown during 5 years (tons)	Lime requirement Jones Method. Pounds CaO per acre
No phosphate	17·6	2700
Rock phosphate	29·4	2520
Super phosphate	31·5	2340
Extra Super	42·2	2250
Ground bone	33·4	2160
Thomas slag	32·7	2070

Again in his Presidential Address to the National Academy of Sciences, India he stated as follows[22]:—

"On the other hand calcium phosphate or phosphate rock is not used as a liming material so far, but as the second and third dissociation constants of phosphoric acid are quite small, when phosphate ions come in contact with hydrogen ions of the soil, HPO_4'' ions and H_2PO_4' ions can be readily formed and hence

calcium or magnesium phosphate can very conveniently be used as a liming material. The solubility in water of $Ca_3(PO_4)_2$ and $CaCO_3$ are of the same order but the solubility of $CaHPO_4$ which is certainly formed in large amounts on the addition of $Ca_3(PO_4)_2$ to acid soils, is less than that of $Ca(HCO_3)_2$. Hence the leaching of calcium compounds from the soil is certainly less when $Ca_3(PO_4)_2$ is added to soil than $CaCO_3$."

Later Dhar and Misra[23] advanced clear and uncontestable evidence regarding the influence of phosphates on the saving of lime. Unpublished data of Dhar and Goel clearly demonstrates the marked effect of H_3PO_4 in lime saving. In America, MacIntire and Shaw[24] have shown by lysimeter experiments that by applying 1000 lbs. of KPO_3 per acre, 636 lbs. of $CaCO_3$ equivalent to lime are saved in 8 years.

The present investigations have been carried on with a view to obtain quantitative results on the value of soluble or sparingly soluble phosphates on the saving of lime in soils. An explanation of the mechanism of lime-saving power of phosphates has been advanced.

EXPERIMENTAL PROCEDURE

25 gms. of normal, good and garden soils of known chemical composition (vide table No. 1) were treated with 150 c. c. phosphate solution, shaken for two hours and the solution was filtered off through a Buchner funnel fitted with filter paper No. 50, after 24 hours. The filtrate was analysed for calcium ions. The treated soils on the Buchner were very carefully transferred to the bottles with distilled water, the volume was made up to 150 c. c. and the mixture was shaken as before. After 24 hours the liquid was filtered off and the filtrate was analysed for calcium. The soil lying on the Buchner was again transferred to a bottle and treated with 150 c. c. distilled water and the procedure was repeated as before. In this way 8 washings were made of each soil. The washed soils were oven dried and the exchangeable calcium was determined by N-NaCl extraction method of Hissink and available phosphate by using 2% citric acid. The results have been reported in terms of pounds of CaO per acre. The apparent densities of normal, good and garden soils are 1·18, 1·12 and 1·20 respectively hence the weight of soils per acre being 2·409 × 10⁶, 2·87 × 10⁶ and 2·45 × 10⁶ lbs./acre respectively. The total of all the washings was taken and the amount of CaO present in the filtrates of the phosphate solutions has been deducted.

To 25 gms. of the above soils 1·25 gms. of $CaHPO_4$, $Ca_3(PO_4)_2$, basic slag and ferric phosphate were added and the amounts of CaO in 8 washings was determined as in the above experiments.

Some experiments were also carried on by adding 0·5 gm. $CaCO_3$, 0·58 gm. $Ca_3(PO_4)_2$ and 0·5 gm. $CaSO_4$ to 25 gms. of normal and good soils either singly or in combination. The same amounts of $CaCO_3$, $Ca_3(PO_4)_2$ and $CaSO_4$ were washed for 8 times with 150 c. c. distilled water and the total CaO in the leachate has been reported. 0·5 gm. $CaCO_3$ was also treated with 150 c. c. of M/100 and M/500 Na_2HPO_4 solution and the amounts of calcium in the washings have been also found out. 0·58 gm. of $CaSiO_3$ was also washed with 150 c. c. water either without any phosphate treatment or treating with M/100 Na_2HPO_4 solution. The results of lime saving have been reported in lbs./acre basis.

RESULTS.

TABLE No. 1.

Composition of soils used in experiments.

Constituents	Total CaO %	Total P_2O_5 %	Total C %	Exchangeable calcium m. e. %	pH	Apparent density
Good soil	4·08	0·418	1·44	15·82	7·6	1·12
Garden soil	2·80	0·122	0·20	8·33	8·0	1·20
Normal soil	1·00	0·079	0·44	12·23	7·6	1·18

TABLE No. 2

Effect of repeated washing with distilled water on CaO, exchangeable calcium etc.

Soils	Amount of lime leached in 8 washings (lbs/acre)	Available P_2O_5 % Originally	Available P_2O_5 % After leaching	Exchangeable calcium in washed soils m. e./100
Good soil ...	5488·0	0·2598	0·2400	15·00
Garden soil ...	5523·4	0·01328	0·0130	7·60
Normal soil ...	3787·0	0·0219	0·0200	11·60

TABLE No. 3

Effect of treating soils with Na₂HPO₄ solution on saving of lime.

	Soils	Good				Garden				Normal			
1.	Concentration of phosphate solution used	M/100	M/500	M/1000	M/5000	M/100	M/500	M/1000	M/5000	M/100	M/500	M/1000	M/5000
2.	Amount of lime saved over control (in lbs./acre)	2949·6	2643·3	2224·7	1920·5	2644	2374	2276·7				1322	962·3
3.	Amount of lime lost when first treated with phosphate solutions (in lbs./acre)	512·2	726·9	772·9	1074	235	244·8	273·2		213·7	240·5	348	509·0
4.	Saving of lime due to phosphate treatment in lbs./acre (2—3)	2437·4	1916·4	1451·8	846·5	2409	2129·2	2003·5		1679·5	1082·5	974	452·3

TABLE No. 4

Effect of treating soils with M/100 NaH$_2$PO$_4$ on the saving of lime

Soils	Good	Garden	Normal
1. Amount of lime saved in 8 washings over control (lbs./acre).	2690·5	2081	1202·8
2. Amount of lime lost when first treated with phosphate solution (lbs./acre)	1280·3	1069	943·0
3. Saving of lime due to phosphate treatment (lbs./acre) (1—2).	1418·2	1012	259·8

TABLE No. 5

Effect of treating the soils with 150 lbs. P$_2$O$_5$ of super phosphate on saving of lime calculated per acre of the soils.

Soils	Good	Garden	Normal
1. Amount of lime taken up from super. solution in lbs./acre.	(−) 1079·4	(−) 440·6	(−) 538·0
2. Amount of lime saved over control (lbs./acre)	2058·4	2261·4	889·0
3. Saving of lime due to super. treatment (lbs./acre)	979·0	1820·8	351·0

Effect of mono-calcium phosphate $CaH_4(PO_4)_2; 2H_2O$ on saving of lime.

Soils	Good			Garden			Normal		
	M/100	M/500	M/1000	M/100	M/500	M/1000	M/100	M/500	M/1000
1. Concentration of phosphate solutions									
2. Amount of lime taken up from phosphate solution in lbs./acre.	2560·6	(-)301	(-)348·8	2223	(-)107·6	(-)284	108·2	0·0	(-)231·0
3. Amount of lime saved over control, lbs./acre.	1676·4	2152	2473·8	909·8	2242·6	2399	1055·4	856·4	1287·0
4. Saving of lime due to phosphate in lbs./acre (2+3)	4237	1851·0	3022·6	3132·8	2135·0	2115	1163·6	856·4	1056

Effect of adding sparingly soluble phosphates (5%) on saving of lime.

Amount of lime in lbs./acre in 8 washings

Soils	Soils + phosphates				Basic slag alone	$Ca_3(PO_4)_2$ alone	$CaHPO_4$ alone
	Basic slag	$Ca_3(PO_4)_2$	$CaHPO_4$	$FePO_4$			
Good	6168·0	2927·0	2515·7	3087·4			
Garden	5068·0	2031·8	2644·0	2668·0	6092·8	4211·2	2943·3
Normal	4138·0	601·4	817·3	1057·0			

Effect of treating soils with phosphates and subsequent leaching with water on the exchangeable calcium and available phosphate.

(a) Using Na_2HPO_4.

Concentrations	Exchangeable calcium m.e./100				Available P_2O_5 %			
	M/100	M/500	M/1000	M/5000	M/100	M/500	M/1000	M/5000
Good soil ...	13·7	14·7	15·1	15·4	0·3695	0·3621	0·3100	0·2694
Garden soil ...	8·10	7·8	8·6	8·3	0·1278	0·0265	0·01668	...
Normal soil ...	11·4	11·6	11·9	11·95	0·2171	0·0632	0·0513	0·0401

(b) Using $CaH_4(PO_4)_2, 2H_2O$.

	Exchangeable calcium m.e./100			Available P_2O_5 %		
	M/100	M/500	M/1000	M/100	M/500	M/1000
Good soil ...	14·96	15·20	15·9	0·2768	0·2335	0·2176
Garden soil ...	8·10	8·30	8·5	0·0523	0·0271	0·0150
Normal soil ...	11·73	11·38	12·4	0·0595	0·0413	0·0356

(c) Using super, basic slag, $FePO_4$, $Ca_3(PO_4)_2$, $CaHPO_4$ etc.

Phosphates added	Exchangeable calcium m.e./100					Available P_2O_5 %				
	Super	Basic slag	$Ca_3(PO_4)_2$	$CaHPO_4$	$FePO_4$	Super	Basic slag	$Ca_3(PO_4)_2$	$CaHPO_4$	$FePO_4$
Good soil ...	14·93	18·36	16·3	13·75	61·1	0·2626	0·269	1·1568	1·087	1·88
Garden soil ...	7·4	10·70	7·3	8·1	8·00	0·0142	0·258	1·098	1·528	1·40
Normal soil ...	11·05	16·83	10·2	11·0	11·3	0·0309	0·276	1·273	1·279	1·21

Amount of lime given out in 8 washings and saving of lime using CaCO₃, Ca₃(PO₄)₂ and CaCO₃+Ca₃(PO₄)₂.

	25 gms. Normal soil				0·5 gm. $CaCO_3$ alone	0·58 gm. $Ca_3(PO_4)_2$ alone	0·5 gm. $CaCO_3$ + 0·58 gm. $Ca_3(PO_4)_2$
	Alone	+ 0·58 gm. $Ca_3(PO_4)_2$	$Ca_3(PO_4)_2$ + $CaCO_3$	+ 0·5 gm. $CaCO_3$			
	1	2	3	4	5	6	7
Amount of CaO given out in 8 washing (in gms. per 25 gms. of soil).	0·0393	0·04605	0·04981	0·03859	0·01887	0·02684	0·03608
Excess of CaO over control ...		0·00675 (2—1)	0·0105 (3—1)	(-)0·00071 (4—1)			
Deficit in CaO from 5, 6 or 7 (gms.) ...		0·02009	0·02558	0·01958			
Lime saved in lbs. acre		1924·6	2461·6	1884·2			
Exchangeable calcium in washed soils (m.e./100)	11·6	12·16	11·30	11·33			

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TABLE No. 10

Amount of lime given out in 8 washings and saving of lime using CaSO₄, Ca₃(PO₄)₂ etc.

	Alone	+ 0.5 gm. CaSO₄	0.5 gm. CaSO₄ + 0.58 gm. Ca₃(PO₄)₂	+ 0.58 gm. Ca₃(PO₄)₂	0.5 gm. CaSO₄ alone	0.5 gm. CaSO₄ + 0.58 gm. Ca₃(PO₄)₂	0.58 gm. Ca₃(PO₄)₂ alone
	1	2	3	4	5	6	7
Amount of calcium oxide given out in 8 washings per 25 gms. of soil (in gms.)							
Normal soil	0·0393	0·19761	0·19851	0·04605	0·1643	0·1843	0·02684
Good soil	0·0600	0·19150	0·2060	0·0618			
Excess of CaO over Control							
Normal soil	—	0·15737	0·1592	0·00675			
Good soil	—	0·13000	0·1460	0·00180			
Deficit of CaO from 5, 6 or 7							
Normal soil	—	0·0070	0·0250	0·02009			
Good soil	—	0·0343	0·0383	0·02300			
Lime saved in lbs/acre							
Normal soil	—	673·6	2405·7	1924·6			
Good soil	—	3177·3	3504·0	2388·0			
Exchangeable calcium in washed soils (m.e./100)							
Normal soil	11·6	12·0	11·33	12·16			
Good soil	15·0	16·17	15·50	16·00			

DISCUSSION

The calcium in solution from soils can come from three different sources : —

1. Soluble forms such as nitrate, chloride, bicarbonate, nitrite and mono-phosphate of calcium.

2. Less soluble forms, such as $CaSO_4$, $Ca_3(PO_4)_2$, $CaHPO_4$, $CaCO_3$, $CaSiO_3$ and other hydroxy or carbonatoapatite formed by $CaCO_3$ and phosphate mixtures.

3. Exchangeable calcium.

There are very little nitrate, chloride, nitrite and mono-phosphate ions in the soluble form and being very soluble are washed out in the first leaching but $Ca(HCO_3)_2$ is formed in the system by the action of CO_2 present in soils. $CaSO_4$, $Ca_3(PO_4)_2$, $CaHPO_4$, $CaCO_3$ and $CaSiO_3$ are sparingly soluble but they are hydrolysed considerably in water and can supply calcium ions. We[23] have already reported that when soils are washed, calcium ions are given out but the amount gradually decreases when the washing is continued. The losses are greater from soils rich in CaO. At the same time high organic matter content and phosphate status were found to reduce the leaching of calcium form soils. As there is a definite decrease in the exchangeable calcium of the washed soils, it appears that a certain amount of calcium is washed from the exchangeable calcium content of the soils. But how much calcium is given out from each of the three sources is not clear.

From a careful study of the tables 1 and 2, it appears that in exchangeable calcium there is a decrease of 0·8, 0·7 and 0·6 m.e. in the good, garden and normal soils respectively. This amount when calculated in pounds per acre comes to nearly 501, 439, 322 respectively but the total losses with water alone from the respective soils are 5488, 5523·4 and 3787 pounds per acre as shown in table 2. Hence it is clear that hardly 10 of the losses can be accounted to the loss of calcium from the exchange-complex of the soil. The remaining 90 has to be attributed to $CaCO_3$, calcium phosphates, $CaSO_4$ or $CaSiO_3$ present in the soil. If the difference between the first and second washings is taken as the loss due to soluble forms of calcium like nitrate, chloride etc. 1 m.e. i.e. 600 lbs. i.e. 12-16 more of total calcium lost can be accounted for. Thus about 75-80% of calcium remains unaccounted for. This may be derived from $CaSO_4$ calcium phosphates, $CaCO_3$ and $CaSiO_3$ present in the soils. As there is very little phosphate in the water extracts of the soils, very little of calcium can be assumed to come from calcium phosphates. Thus $CaSO_4$, $CaCO_3$ and $CaSiO_3$ remain as the chief sources of calcium release. This is evident from tables 9 and 10. We have observed that $CaCO_3$ checks the hydrolysis of $Ca_3(PO_4)_2$ resulting in decrease of phosphate ions in solution but as it is clear from the amounts of CaO given in table 9, the amount of CaO does not decrease very much when $CaCO_3$ and $Ca_3(PO_4)_2$ are mixed together and is approximately equal to the sums obtained from their separately solubilities. When $CaCO_3$ or $Ca_3(PO_4)_2$ are mixed with the soil singly or in combination, there is always smaller amounts of CaO in the filtrates than the amounts expected to come into soluble forms. Thus $CaCO_3$ and $Ca_3(PO_4)_2$ interact and smaller amounts of lime are leached away but they form the main sources of calcium washed away in successive water extracts.

By adding soluble phosphates like Na_2HPO_4, there is a marked saving of lime which very clearly points out the special function of phosphates in checking the loss

of lime by leaching. The added phosphates can react with the soil constituents in the following manner :—

(a) Some soluble phosphate reacts with $CaCO_3$ present in the soils to form sparingly soluble phosphates like $CaHPO_4$, $Ca_3(PO_4)_2$, $Ca_3PO_4)_2$. $CaCO_3$ and $Ca_3(PO_4)_2$. $Ca(OH)_2$.

(b) Some of the soluble phosphates react with the sesquioxides (iron and aluminium and titaninum hydroxides) and fixation of phosphate take place.

(c) Some of the soluble phosphate reacts with the exchangeable calcium and gets fixed as sparingly soluble $CaHPO_4$ thereby decreasing the exchangeable calcium of the system.

(d) It has been observed that, when soils are treated with phosphate solutions from concentrated solutions not more than 50% of the added phosphate is absorbed whilst from dilute solutions almost complete adsorption of the phosphate can take place.

As pointed out the main sources of calcium loss from soils seem to be (a) exchangeable calcium and (b) $CaCO_3$ present in the soil. The added phosphate reacts with these two sources, making calcium inactive and less soluble and thus checking the loss. These views are supported from the experimental observation regarding exchangeable calcium in the phosphate-treated soils as recorded in table 8 (a), (b) and (c). The results recorded show a marked decrease of exchangeable calcium. It is well known that when soils are repeatedly washed with water, there is also a decrease of exchangeable calcium in the soil but when the same soil, before washing is treated with phosphates, there is an immediate decrease in the exchangeable calcium. Hence smaller amounts of calcium are leached out and there is a saving of lime. The effect of soluble phosphates on $CaCO_3$ and $CaSiO_3$ has also been studied separately and it has been observed that from the phosphated samples there is lesser leaching of calcium as is evident from the following data :—

1. 0·5 gm. $CaCO_3$ alone with 150 c.c. water gives out in 8 washings ... ... 0·01897 gm. CaO

2. 0·5 gm. $CaCO_3$ treated with M/100 Na_2HPO_4 (150 c.c.) and then washed with water for 8 times loses ... 0·01368 gm. CaO

3. 0·5 gm. $CaCO_3$ treated with M/500 Na_2HPO_4 and then washed with water in the same way loses ... 0·01398 gm. CaO

4. 0·58 gm. $CaSiO_3$ alone with 150 c.c. water gives out in 8 washings ... ... 0·025 gm. CaO

5. 0·58 gm. $CaSiO_3$ treated with M/100 Na_2HPO_4 solution (150 c.c.) and then washed with water for 8 times loses 0·0160 gm. CaO

The saving of CaO by 2% $CaCO_3$ on treatment with phosphate thus saves about 448 lbs. of lime per acre while the silicate of calcium on phosphate treatment seems to save lime double of this amount. It has also been found that the phosphate treated $CaCO_3$ loses its phosphate completely in 8 washings, hence the saving of lime

can not be expected to last long. In our experiments on saving of lime by phosphate treatment to soils, a similar phenomenon has been observed where the loss of lime after 4 or 5 washings from the untreated and phosphate treated soils is approximately the same. But in the soils the adsorption of phosphate being shared by several constituents, the removal of phosphates is a much slower process.

The lime saving by phosphate treatment is not directly proportional to the concentrations of phosphate used. As shown in table 3, in good soil treated with $M/100$ Na_2HPO_4, there is a saving of 2437·4 lbs. of lime, whilst with $M/5000$, a saving of 846·5 lbs. of lime takes place. Thus when the concentration of the soluble phosphate is only 1/50th of the former, the lime saved is $\frac{1}{3}$ in the more dilute solution. This may be due to greater amounts of phosphate being adsorbed by the soil at lower concentrations.

The amount of phosphate added at $M/5000$ Na_2HPO_4 is about 150 lbs. of P_2O_5. If this amount of phosphate combines wholly with calcium to form $Ca_3(PO_4)_2$, $CaHPO_4$ or higher phosphates, the amount of calcium saved should have not been greater than 224 or even 448 lbs. of lime. Thus the effect of soluble phosphates seems to be very interesting. The phosphates seems to inactivate a part of exchangeable calcium, $CaCO_3$, $CaSiO_3$ and the presence of organic matter and sesquioxides etc. in the soils by adsorbing the calcium ions oppose leaching of lime by water.

On adding sparingly soluble phosphates like $Ca_3(PO_4)_2$ and $CaHPO_4$, small amounts of calcium and phosphate ions are given out. Hence there is an increase in the concentration of calcium ions in the filtrates, but the phosphate ions help in the retention of calcium in the soil and there is a definite saving of lime of the soils as is clear from tables 9 and 10. The addition of $CaSO_4$ appears to save lime while the saving is greater when $CaSO_4$ is mixed to the soils with $Ca_3(PO_4)_2$. Similarly $CaCO_3$ and basic slag when mixed with the soil appear to save lime because the SO_4'' and CO_3'' ions from $CaSO_4$ and $CaCO_3$ or basic slag react with calcium ions in solution to form $CaCO_3$ and $CaSO_4$ at the surface of soil particles, which are less soluble than $Ca(HCO_3)_2$. The phosphate ions liberated by the hydrolysis of $FePO_4$, $Ca_3(PO_4)_2$ and $CaHPO_4$ are adsorbed at the surface of $CaCO_3$ and soil particles to prevent the loss of lime.

In an earlier communication[25] we had proposed that as the third dissociation constant of phosphoric acid is smaller than the dissociation constant of carbonic acid, hence the possibility of the formation of $Ca(HCO_3)_2$ is less than that of $CaHPO_4$ which is less soluble than $Ca(HCO_3)_2$. Hence there is a saving of lime in presence of phosphate. The present investigations not only support this view but also explain the decrease in exchangeable calcium by phosphate treatment and at the same time the marked effect on lime saving. The peculiar behaviour of monocalcium phosphate also supports this view where inspite of a large adsorption of calcium ions the exchangeable calcium decreases and the saving of lime from soil is greater at low concentrations. This is due to the fact that the adsorbed calcium ions at higher concentration are themselves liberated causing a smaller saving of lime.

Our results on the saving of lime by the application of phosphate to soils explain the decrease in lime requirements obtained by Burgess[26] by the use of basic slag, rock phosphate and even super phosphate. That a liberal application of phosphate with manure in cold countries may eliminate the need for liming even under very acid soil conditions as observed by Aslander[27] in Sweden is in accordance to our observations and conclusions.

SUMMARY

The additions of soluble phosphate of sodium save a considerable amount of lime from soils on washing because of the formation of $CaHPO_4$ in preference to the production of $Ca(HCO_3)_2$ which is much more soluble than $CaHPO_4$. The sparingly soluble phosphates like basic slag, tricalcium phosphate, dicalcium phosphate and ferric phosphate have been observed to save lime. The addition of $CaCO_3$ and $Ca_3(PO_4)_2$ in combination also saves lime but the amount is smaller because these materials themselves furnish calcium ions which are lost on washing. The exchangeable calcium of the phosphate treated soils is always smaller than in the original soils. Various calculations regarding the loss of lime from different sources have been put forward to explain the loss of lime supporting our view of saving of lime on the grounds of dissociation constants of phosphoric acid.

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COMPOSITION OF DIFFERENT TYPES OF BONE MEALS AND EFFECT OF PARTICLE SIZE ON THE AVAILABLE PHOS-PHORIC ACID CONTENT

By

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Fertilizer use in India has of late been showing progressive increase, the trend being naturally more baised towards nitrogenous fertilizers which can make good the primary deficiency in Indian Soils. Close in importance to this however, is the element phosphorus, deficiency of which prevails in tracts of Hyderabad. Madras, Mysore, Orissa, Bengal, Assam and Bombay States, on which application of phosphatic fertilizers along with nitrogen is already showing significant response. It must be anticipated that in the remaining soil regions also, the existing reserves of phosphorus will be getting depleted with increased crop yields obtained with nitrogenous fertilizers. The increasing stress on cultivated lands for high crop production in the future developmental plans calls for timely recognition of the role that phosphatic fertilizers will play, immediately next in importance to that of nitrogenous fertilizers.

TYPES OF PHOSPHATIC MATERIALS USED AS FERTILIZERS

Phosphatic materials used as fertilizers contain phosphorus in different chemical forms of varying solubilities. The chief phosphatic fertilizer used in India has been the single super phosphate which carries phosphorus in the form of mono calcium phosphate, soluble in water. The response obtained by proper application of the material constitutes a standard with which other fertilizers of the type are compared. Fixation of water soluble phosphorus compounds in soil and soil reaction however affect the utilization of phosphorus by plants from such fertilizers, which restricts the scope of super phosphate to soils of reaction not below pH 6 or exceeding 7·5 and containing no abnormal amounts of lime or a high proportion of reactive clay. The scope at this stage therefore requires to be expanded for utilization of phosphatic materials that carry phosphorus in forms soluble in ammonium citrate, which have been shown by laboratory and field tests to have a wider application without any significant loss of efficiency as sources of assimable phosphorus for plants. Trials conducted at the Indian Agricultural Research Institute with dicalcium phosphate, now being manufactured on a small scale in the country, have shown that the fertilizer is as efficient as superphosphate on neutral and calcarious soils. Tests on acid soils are in progress.

SCOPE FOR BONE MEALS

One of the important natural sources of a fertilizer material of this type available in the country is raw bone meal obtained as a by product from the bone crushing industry. The annual collection of bones in India is estimated at 150,000

tons. The yield of bone meal of particle size less than 3/32 inch which is banned for export amounts to about 20% of the original bones. Raw bone meals may contain 3·4% organic nitrogen, which adds to its fertilizing value but in the normal doses applied this requires to be supplemented by additional applications of nitrogen for optimum crop growth. Phosphorus for which bone meal is primarily valued, is combined with calcium as tricalcium compound scattered through an organic matrix. The easy solubility of this in mineral acids and some concentrated salt solutions, however, distinguish it from tricalcium phosphate present in naturally occuring rockes and other materials. The insolubility of rock phosphate is attributed to the apatitie combination with fluorine. In bone, fluorine is replaced by carbonate and calcium and partly by sodium and magnesium which accounts for its solubility and availability to plants.

TYPES OF BONE MEAL

The product obtained directly from the crushing of bones is known as 'Raw bone meal'. This contains 3·4% nitrogen and about 21% of total P_2O_5, corresponding to the original composition of bones. Processing of bones by the action of steam under pressure removes glue, fat and the nitrogenous gelatinous matter and renders bones easily friable, The 'Steamed bone meal' contains 1-2% nitrogen and about 27% P_2O_5 and is highly valued both as a fertilizer as well as a cattle feed. Partial steaming may also render bones friable by disengaging the glue and gelatinous compounds without their actual removal. The Steam Processed bone meal is a product similar in composition to the raw bone meal but of greater finness of the size of particles.

EXPERIMENTAL

The availability of phosphate for plants in materials of this type is generally assessed in the laboratory by their solubility in neutral ammonium citrate solution, Wagner (1899) working with basic slags suggested extraction with 2% citric acid solution for the estimation of available P_2O_5, based on a high correlation of the figure with actual plant uptake and growth. Jacob et al (1931, 1935, 1936) and Kitswa and Salter (1931) have reported evidence to show that the 2% citric acid extraction gives a better index of the nutrient value of steamed bone meal than ammonium citrate.

Availability of phosphorus in bone meals is greatly influenced by the finness of particles to which they are ground. A detailed examination of the composition of different types of bone meals, effect of particle size on available P_2O_5 content and comparison of available P_2O_5 contents obtained by ammonium citrate and citric acid extractions has been carried out in the present investigation.

RESULTS

Composition of different types of bone meals.

The following table gives variations in the chemical composition observed in samples of commercial 'raw bone meal', 'steamed bone meal' and 'processed bone meal':

TABLE I

Chemical Composition of different bone meals.

		Raw bone meal			Steamed bone meal			Processed bone meal	
		1	2	3	1	2		1	2
Moisture	...	6·6	5·0	7·7	3·4	3·5	...	4·2	4·8
Loss on ignition	...	38·8	...	31·8	26·0	...	...	34·1	33·4
Ash	...	62·2	...	68·2	74·0	...	...	65·9	66·6
Insoluble Silica	...	0·3	...	1·1	0·29	...	...	0·7	0·9
Nitrogen	...	4·1	3·9	4·1	2·8	1·75	...	4·0	3·5
Total, P_2O_5	...	22·9	26·0	21·6	27·7	28·8	...	24·4	25·9

In the samples examined, nitrogen content in raw bone meal was found to be around 4%. This is perhaps the upper limit of nitrogen in bone meal, as well decomposed bones have been reported to yield bone meal of less than 3% nitrogen. The phosphoric acid content of raw bone meal is of the order of 21-23% but one of the samples examined was found to contain as high as 26% P_2O_5. This exceptional sample may have been derived from selected pieces of shaft bones which are richer in phosphorus.

Nitrogen content in steamed bone meal may vary from 1·75 to 2·8% while the phosphoric acid content is of the order of 27 to 29%.

The processed bone meals prepared by partial steaming of bones was found to contain somewhat higher amounts of nitrogen up to 4·8%, due to partial removal of some non nitrogenous materials. The phosphoric acid content was also correspondingly higher than that of raw bone meal, and of the order of 24—26%.

Effect of particle size on availability of P_2O_5 in bone meals

The solubility of phosphoric acid in different types of bone meals as affected by particle size was determined in neutral ammonium citrate and 2% citric acid solutions. The data obtained are given in the following tables.

Available P_2O_5 in gm per 100g of sample

Raw bone meal $\left(\begin{array}{l} \text{I :—21·6 % } P_2O_5 \\ \text{II :—26·0 % } P_2O_5 \end{array}\right)$

Finness of Particles	Amm. Citrate.		Citric acid.	
	I	II	I	II
$\frac{3}{32}$ inch.	4·79	10·75	7·41	13·9
$\frac{1}{25}$,,	9·98	...	12·04	...
$\frac{1}{60}$,,	13·62	17·45	16·24	19·5
$\frac{1}{100}$,,	16·46	19·90	19·64	22·6

Steamed bone meal (28·8 % P_2O_5)

$\frac{1}{10}$ inches	14·51	15·50
$\frac{1}{60}$,,	19·72	26·80
$\frac{1}{100}$,,	19·41	27·70
$\frac{1}{150}$,,	19·40	28·40
$\frac{1}{200}$,,	19·30	28·40

Steam processed bone meal $\left(\begin{array}{l}\text{I :—}24·4 \% \ P_2O_5\\ \text{II :—}25·9 \% \ P_2O_5\end{array}\right)$

	I	II	I	II
$\frac{3}{32}$,,	8·60	11·31	15·8	13·43
$\frac{1}{25}$,,	14·28	17·30	19·79	20·26
$\frac{1}{60}$,,	16·38	18·42	22·30	23·25
$\frac{1}{100}$,,	17·12	20·33	23·04	23·90

The data presented shows that the normal raw bone meal may carry only about 34 % of the total P_2O_5 in available form. The exceptional sample II showed an available P_2O_5 content of about 53 % of the total of 26. It is significant to observe that the availability of phosphorus in bone meal is markedly increased to 75-87 % of the total, merely by grinding to particle size below 1/60 inch. This indicates that the chemical nature of the phosphorus compounds even in raw bone meal is such as would enable plants to assimilate the nutrient and the low efficiency of the normal bone meal of 3/32 inch is mainly due to the small physical suface exposed to plant roots.

Steamed bone meal at particle size of 1/10 inch is comparatively richer in available P_2O_5 content due possibly to the removal of gummy and gelatinous matter which make the material porous. Grinding to particle size of 1/60 inch increased the available P_2O_5 content from 53 % of the total to about 93%. It has been shown to be possible to obtain nearly 99% of the total P_2O_5 in available from by grinding this to a finness of 1/150 inch.

The steam processed bone meal has been shown to carry about 65% of the total P_2O_5 in available form at particle size of 3/32 inch, even though the process does not involve any material extraction of the gum and gelatine. The changes brought about however, render the bones easily friable which may account for higher efficiency of this type of material than raw bone meal. Grinding this to a finness of 1/60 inch makes nearly 90% of the total phosphorus available.

The vulues for P_2O_5 soluble in the two extractants show that the 2% citric acid extraction yields higher amounts than neutral ammonium citrate. For normal bone meal the value of 34% of the total being in available form, as indicated by citric acid extraction, corresponds to observations of other workers and would appear to provide a better index than the ammonium citrate value of 22%. The steamed bone meal provides further evidence that when ground to the highest finness of particle size, the citric acid soluble value of 99% of the total is a better indication of the fertilizer value of the material. These results however require to be confirmed by plant tests.

SUMMARY

Fuller exploitation of indigenous bone meal for use as a phosphatic fertilizer in combination with nitrogen, would appear to provide a fruitful field for increased crop production in the country. The present investigation shows that the normal raw bone meal of particle size less than 3/32 inch may carry only about one-third of the total phosphorus in available form. The efficiency can be considerably increased by grinding to a higher finness of about 1/60 inch but the operation would be rather difficult. Steamed bone meal can easily be ground to a finness of 1/60 inch at which stage the material may yield about 90% of the total phosphorus utilizable by plants.

Partial steaming of bones without extraction of glue and gelatine, provides an alternate processing treatment in which the original nitrogen as well as phosphoric acid contents are retained and the product can be easily pulverized to a finness of 1/60 inch containing 90% of the total phosphorus in available form.

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EFFECT OF DIFFERENT PHOSPHATES ON THE MANURIAL VALUE OF ANAEROBICALLY FERMENTED COWDUNG IN THE PRODUCTION OF COMBUSTIBLE GAS

By

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Production of combustible gas from anaerobic fermentation of cowdung (Desai and Biswas 1945), has, of late, attracted considerable attention in the country. The scope of use of fresh slurry as manure is, however, limited since the semi-fluid mass cannot be carried through drains to fields at very large distance from the gas plant and necessarily, the material has to be dried or stored for use any time it is required. Drying of the material may involve loss of large amounts of ammonia formed from nitrogenous compounds in the fresh cowdung by anaerobic fermentation (Hutchinson 1916), and hence, may decrease the manurial value of the material.

Very little information regarding the manurial value of such dried fermented cowding is, however available. Desai and Biswas (loc. cit.) showed that the fermented cowdung had greater rate of nitrification than farm yard manure though it was still much less than that of most organic manures like oil cakes. Addition of phosphates to soils had been known to stimulate nitrification (Peterson and Scott 1913; Fraps 1920; Brown and Gowda 1924; Fraps and Sterges 1938) and it was considered worth-while to see if the nitrifiability of the dried slurry could be enhanced by incorporation of different phosphates with cowdung undergoing fermentation or if the quality of the manure could otherwise be improved (Hutchinson 1923). Greater solubilisation and higher availability of the indigenous phosphates like Singbhum phosphate or Trichi nodules were also considered possible (Bhaskaran, Pillai and Subrahmanyan 1938). Incidentally, the production of gas under treatment of cowdung with different phosphates was noted and the observations recorded in the present report.

MATERIALS AND METHODS

Soil—Delhi soil, a sandy loam was collected up to the depth of 9 inches and was air dried, sieved through a 2 m.m. sieve and used in the experiments. The composition of the soil is given in the Appendix I.

Manures —Nitrification of the following manures was studied during the present investigation:

1. Dried cowdung

2. Mustard cake

3. Ammonium sulphate

4. Fermented cowdung without any treatment

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5. Fermented cowdung with 1 per cent superphosphate

6. Fermented cowdung with 1 per cent bone meal

7. Fermented cowdung with 1 per cent
    Singbhum phosphate

8. Fermented cowdung with 1 per cent
    Trichi nodules

The composition of the manures is given in the Appendices II and IIA, and that of the phosphatic materials in Appendix III.

Methods; Production of manure and combustible gas from cowdung—150 lbs of fresh cowdung were mixed equal quantity of water and then put in, for fermentation in the digestion tank of the Fuel Gas Plant used by Desai and Biswas (loc. cit.). In the case of the treatments, 1·5 lbs of powdered phosphate were mixed with the material in the digestion tank. Production of gas was allowed to continue for 15 days at the end of which it fell considerably. It was noted daily. The slurry was taken out after 15 days of fermentation, dried in the sun, powdered and sampled. The powdered samples were analysed for nitrogen and total and available phosphate and were used during the nitrification studies. Each series of treatments was repeated thrice and samples of manures obtained in each case were separately used in the nitrification studies.

Nitrification.—The manures were mixed with soil in such proportions as to add 30 mg. of nitrogen per 100 gms of soil (Walton 1928). The mixtures were moistened to one third their saturation capacities and incubated at 30°C for a period of 12 weeks. Ammoniacal, nitrite and nitrate nitrogen contents of the mixtures were determined at intervals of two weeks and loss of moisture made up by adding distilled water from time to time. The total nitrogen contents of the mixtures were determined at start and at the end of twelve weeks.

Total nitrogen, nitrite, nitrate and total P_2O_5 contents of the mixtures and of phosphates were determined by the usual methods (Wright 1934). Estimation of the ammoniacal nitrogen was carried out by McClean and Robinson's method (1924). Organic carbon contents of the manures were obtained from loss on ignition. Water soluble P_2O_5 contents were estimatud by evaporating a definite aliquot of 1:10 extracts of the manures and oxidising the residue by H_2O_5, P_2O_5 content of which was estimated separately to be subtracted from the total figures of P_2O_5 obtained.

Pot experiments—Pot experiments were carried out using 10 lbs of soil with the manures so as to supply 50 lbs of effective nitrogen per acre. Each treatment had five replications. Paddy was grown in summer and pea in winter.

RESULTS

Contents of ammoniacal, nitrite and nitrate nitrogen contents of Delhi soil, untreated and treated with cowdung, mustard cake, ammonium sulphate and fermented manures during different periods are given in Table I.

[361]

TABLE I

Ammonia, nitrite and nitrate in Delhi soil under different treatments
during different periods

Expressed as mg per cent on air dry soil

	At start	2 weeks	4 weeks	6 weeks	8 weeks	12 weeks
Delhi soil without treatment						
NH_4—N	3·78	3·78	2·27	3·78	3·03	5·30
NO_2—N	tr	0·02	tr	tr	tr	...
NO_3—N	0·51	1·02	1·36	1·70	1·67	2·38
Delhi soil with dried cowdung						
NH_4—N	4·33±·12	3·43±·14	3·78±·24	3·03±·15	4·05±·18	4·30±·02
NO_2—N	tr	tr	0·02±·04	0·01·±·00	0·03±·01	0·02±·01
NO_3—N	0·32±·01	1·02±·01	1·78±·15	2·40±·24	3·02±·18	3·78±·15
Delhi soil with mustard cake						
NH_4—N	3·78±·00	4·54±·14	2·27±·12	3·78±·14	3·78±·19	6·06±12
NO_2—N	tr	tr	0·11±·02	tr	0·04±·06	tr
NO_3—N	0·34±·15	9·55±·19	13·63±·25	16·36±·04	16·36±·04	17·70±·04
Delhi soil with ammonium sulphate						
NH_4—N	30·80±1·24	6·06±·12	4·54±·24	4·16±·12	5·30±·02	7·58±·05
NO_2—N	0·04± ·02	0·02±·02	0·02±·01	0·02±·02	0·04±·12	tr
NO_3—N	1·02± ·15	16·36±·08	24·54±·25	27·27±·18	27·27±·24	27·27±·12
Delhi soil with fermented cowdung without treatment						
NH_4—N	4·03±·14	4·03±·14	3·03±·24	4·03±·14	4·54±·24	3·78±·00
NO_2—N	0·01±·00	tr	0·04±·00	...	tr	...
NO_3—N	0·57±·13	tr	0·58±·19	0·34±·11	0·62±·17	0·82±·23
Delhi soil with cowdung fermented with superphosphate						
NH_4—N	4·03±·14	4·29±·14	2·53±·14	3·28±·14	3·53±·14	4·17±·44
NO_2—N	0·01±·00	tr	0·04±·02	tr	tr	tr
NO_3-N	0·28±·08	0·34±·19	0·45±·25	0·34±·19	0·56± 16	0·97±·27
Delhi soil with cowdung fermented with bone meal						
NH_4—N	4·03±·14	3·53±·14	2·78±·27	3·78±·00	3·78±·28	4·04±·56
NO_3—N	0·01±·00	0·01±·00	0·04±·02	...	0·02±·01	...
NO_3—N	0·57±·03	tr	0·68±·19	0·57±·17	0·51±·23	0·82±·23
Delhi soil with cowdung fermented with Singbhum phosphate						
NH_4—N	3·91±·18	3·78±·24	2·52±·14	3·28±·14	4·79±·14	3·53±·28
NO_2—N	0·01±·02	tr	0·04±·02	...	tr	...
NO_3—N	0·40±·15	tr	0·34±·19	0·32±·18	0·23±·13	0·41±·22
Delhi soil with cowdung fermented with Trichi nodules						
NH_4—N	3·78±·24	4·03±·14	2·78±·14	3·41±·12	4·29±·14	3·78±·14
NO_2—N	0·01±·03	tr	0·04±·02	...	tr	...
NO_3—N	tr	tr	0·34±·19	0·23±·13	0·17±·19	0·57±·17

Average nitrogen contents of the soil treated with different manures at the start of the experiment and at the end of 12 weeks are given in Table II :

TABLE II

Nitrogen content of the Delhi soil under different treatments in the
beginning and at the end of 12 weeks

Expressed as mg per cent on moisture free soil

Description	At start	After 12 weeks
Soil without treatment ... › ...	56·0	58·0
Soil with dried cowdung	83·0±1·2	85·7±1·1
Soil with mustard cake	85·3±0·2	84·3±0·1
Soil with ammonium sulphate	86·0±0·2	80·7±0·3
Soil with fermented cowdung without any treatment	84·3±0·1	81·7±1·1
Soil with cowdung fermented with superphosphate	83·7±0·2	82·0±0·0
Soil with cowdung fermented with bone meal	83·7±0·2	84·4±1·1
Soil with cowdung fermented with Singbhum phosphate	84·0±0·0	83·0±1·2
Soil with cowdung fermented with Trichi nodules	84·3±0·2	85·0±0·5

Yields of paddy in soil treated with different manures are given in Table III.

TABLE III

Yield of paddy in Delhi soil under different treatments
In gms per pot

Treatment	Grains	Straw
No treatment	6·1±0·3	8·2±0·1
Farm yard manure	7·9±0·4	14·1±1·3
Manure from fermented cowdung without any treatment	7·3±0·5	13·5±14·1
Manure from cowdung fermented with superphosphate	5·1±0·2	8·6±1·0
Manure from cowdung fermented with bone meal	5·0±0·3	10·0±1·2
Manure from cowdung fermented with Singbhum phosphate	4·8±0·2	6·3±0·2
Manure from cowdung fermented with Trichi nodules	5·4±0·2	7·9±1·3

Yields of pea in soil under treatment of different manures are given in Table IV.

[363]

TABLE IV

Yield of pea in Delhi soil under different treatments,

In gms per pot

Treatment	Plants with grains	Grains
No treatment	7·83	3·48
Manure from cowdung fermented without any treatment	10·78	4·99
Manure from cowdung fermented with superphosphate	13·42	6·26
Manure from cowdung fermented with bone meal	15·15	6·93
Manure from cowdung fermented with Singbhum phosphate	12·63	5·90
Manure from cowdung fermented with Trichi nodules	12·65	5·75
S. E m	±0·43	±0·29
C. D. at 5 per cent	1·26	0·86
C. D. at 1 per cent	1·71	1·17

Daily production of gas from fermentation of cowdung with and without different phosphates is given in Table V.

TABLE V

Production of combustible gas from fermentation of 150 lbs of cowdung with and without phosphatic treatments

(average of 15 days)

Treatment	Gas per day (cubic ft)
No treatment	3·01
Superphosphate 1 per cent	3·96
Bone meal 1 per cent	3·72
Singbhum phosphate 1 per cent	3·19
Trichi nodules 1 per cent	4·13
S. E m	±0·40

DISCUSSION OF RESULTS

From the composition of different manures from fermentation of cowdung (Appendix II) it is seen that the nitrogen content of the manures has increased as compared with that of fresh cowdung. This increase is highest in the case of cowdung without any treatment. The general increase in the nitrogen content of the manures is evidently due to the loss of organic carbon in the form of gas. In the case of manures obtained from fermentation with phosphates, the increase in nitrogen contents has been very often less than that in the case of fermentation without phosphates probably because of stimulation of ammonification by phosphates and the loss of ammonia while sundrying.

It is also seen that treatment of cowdung with phosphates has increased the phosphate contents of the dry fermented manures. The fermented manures are, however, devoid of measurably higher amounts of water soluble P_2O_5 than cowdung or fermented cowdung without any treatment. Quite an appreciable amount of phosphate may, at the same time, be used up in building up of the bacterial cells taking part in the fermentation process. This built up phosphate may be available for uptake by crops. This is shown by significant increases in yields of pea on treatment of phosphate treated cowdung (Table IV).

Inspite of the superiority, in composition, of the fermented manures over unfermented cowdung, their rates of nitrification in soil have been found to be singularly low (Table I). It is also seen that treatment of cowdung with phosphates has not improved their nitrifiability. The C/N ratios of the fermented manures are found to be very much lower than the same of the unfermented cowdung (Appendix II A); still this reduction in the ratio does not appear to have improved the rate of nitrification of the manures to any appreciable extent. Compared to ammonium sulphate or mustard cake, the fermented manures offer themselves to be very poor nitrogeneous manures.

It may be possible that in absence of much nitrification in the soil treated with the fermented manures, nitrogen fixation has been taking place with the oxidation of organic carbon by microbiological agencies. The extent of oxidation of organic matter during the period of incubation has not been determined during the investigation. It is certain, however, that no remarkable fixation of nitrogen has taken place in the soil during the period of 12 weeks in any case (Table II).

From their higher phosphate contents, the manures from cowdung fermented with phosphates may be quite considered quite suitable for leguminous crops which do not require readily available nitrogen for their growth. This observation is supported by yields of pea raised from the manures (Table IV). Their low rates of nitrification may, not, however, make them suitable for growth of cereals. This is shown by lack of response, to treatments with these manures, by the paddy crop (Table III).

It is seen from the data in Table V that the differences in gas production between the treatments are not significant.

SUMMARY AND CONCLUSIONS

During the present investigation, studies were made on the effect of adding different phosphates like superphosphate, bone meal, Singbhum phosphate and Trichi nodules to cowdung undergoing anaerobic fermentation with respect to the manurial values of the dry residual materials by nitrification in Delhi soil and also

by actual production of a cereal like paddy and of a legume like pea. Production of combustible gas under such treatments was also noted.

By anaerobic fermentation of cowdung with or without treatments with phosphates, nitrogen content of the manure produced was increased. The manures had also higher P_2O_5 contents under treatment with phosphates.

It was observed that treatments with phosphates did not materially improve the poor nitrifiability of the fermented or unfermented cowdung. This was also shown by poor yields of paddy under the treatments of the manures.

Though there was very little difference in the contents of water soluble P_2O_5 of different manures, pea gave good response to manures obtained from fermented cowdung treated with 1 per cent of different phosphates.

The differences in the production of combustible gas between different phosphatic treatments were not significant.

ACKNOWLEDGEMENT

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Composition of Delhi soil (0-6′)

Constituents expressed as per cent on moisture free basis

Constituent	Per cent
Organic carbon	0·42
Organic nitrogen	·056
Ammoniacal nitrogen	·0032
Nitrite nitrogen	—
Nitrate nitrogen	tr
Total P_2O_5	·07
Coarse sand	41·47
Silt	32·33
Clay	11·94
pH	7·2

APPENDIX II

Composition of manures from fermentation of cowdung
Expressed as per cent on moisture free basis

Description	Nitrogen	Total P_2O_5	Water soluble P_2O_5
Cowdung	1·13±·01	0·810±·003	0·040±·000
Manure from fermentation of cow-dung	1·41±·03	·873±·004	·053±·002
Cowdung with superphosphate ...	1·28±·03	1·750±·009	·043±·002
Cowdung with bone meal ...	1·28±·03	2·160±·019	·046±·004
Cowdung with Singbhum phosphate	1·43±·07	2·143±·005	·043±·002
Cowdung with Trichi nodule ...	1·37±·04	2·123±·015	·043±·004

Composition of manures from fermentation of cowdung

Expressed as per cent on moisture free basis

Description	Loss on ignition	Organic carbon	C/N
Cowdung	74·00±·52	43·02±·41	38·0±0·4
Manure from fermentation of Cowdung	60·18±·24	34·99±·14	25·0±0·6
Cowdung with superphosphate ...	53·51±·35	31·11±·20	24·3±0·5
Cowdung with bone meal ...	49·45±·52	28·80±·30	22·7±0·4
Cowdung with Singbhum phosphate	65·17±·56	37·87±·32	26·7±1·0
Cowdung with Trichi nodules ...	65·78±·43	38·24±·25	25·3±1·3

APPENDIX III

Average composition of the phosphates

Expressed as per cent on moisture free basis

Phosphate	Nitrogen	Total P_2O_5	Water soluble P_2O_5
Superphosphate	0·60	15·30	11·60
Bone meal	3·74	23·20	0·39
Singbhum phosphate	0·40	21·90	0·27
Trichi nodule	0·10	21·60	0·23

APPLICATION OF HIGH LEVELS OF PHOSPHATES TO RED SOILS—STUDIES ON THEIR EFFECT ON PHOSPHORUS STATUS AND CROP YIELDS

By

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Under the conditions of soils obtaining in this Country, responses of crops to different nutrients show marked differences depending both upon crop type and nature of the plant nutrient. Quick and immediate responses are obtained to nitrogen fertilization under a wide variety of soil conditions, while response to phosphate manuring, particularly of Cereals is only moderate and in many cases not noticeable. Phosphates in combination with nitrogen show a higher degree of response than with phosphates alone[1]. The poor response to phosphate fertilization is surprising considering the generally low phosphate status of our soils and this is commonly assumed to be due to high fixation in these soils. To off-set this fixation and increase the availability of phosphates to crops, various measures like mixing the phosphate with organic matter and composts, placement at depth and others are recommended [2,3,4]. Application of large doses of phosphates within economic limits appears to offer one method of overcoming fixation, while simultaneously building up the phosphate reserves in the soil.

Phosphates have a big influence on root development and consequently of value in growth of rain fed dry crops, where such development can help to offset the disadvantages of moisture insufficiency in the soil. Owing to this benefit being less conspicuous, phosphate fertilization is popularly believed to be uneconomical in raising dry crops. With a view to investigate the possibility of building up the phosphate status in soils through saturation fertilization and make them available to unirrigated crops, investigations were taken up by us to apply increasing doses of phosphate periodically over a number of seasons and follow the results of these treatments on the phosphate distribution in the soil and the crop yields. Included in this work are the analysis of each of the crops and assessment of the uptake of Nitrogen and Phosphorus from the soil.

EXPERIMENTAL

The soil selected for these studies is a red sandy loam, typical of the soils distributed in the District of Bangalore and the surrounding areas. The rainfall in this region is in the range of 25—30 inches per annum. The soil is nearly neutral in reaction, low in nitrogen and organic matter and poor in phosphoric acid and lime, though moderately high in potash. In actual distribution, the soil occurs frequently in great depths ranging from 4 to 6 feet, while the average depth is well over one foot. These soils are believed to be derived from the granites typically present in the area.

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The analytical details relating to the physical and chemical constituents are given below:

Mechanical Analysis:

		% on Moisture free basis
Coarse sand	...	38·86
Fine sand	...	32·35
Silt	...	5·89
Clay	...	19·68
Organic matter	...	1·15

Chemical Analysis:

pH	...	6·8	
Total N	...	0·063	percent.
Total P_2O_5	...	0·054	,,
Citric soluble P_2O_5	...	0·014	,,
Total CaO	...	0·22	,,
Exchangeable CaO	...	0·15	,,
Total K_2O	...	0·09	,,
Exchangeable K_2O	...	0·005	,,

The crop selected for these studies is the millet Ragi (Eleucine Coracana) which is grown extensively over these soils under rainfed conditions. This is a hardy crop grown under both dry and irrigated conditions, and is known to respond to phosphate fertilization better than paddy, which is the other important cereal crop grown here. Ragi was grown in regularly laid out one square yard plots, each plot being planted with 36 seedlings and receiving uniform cultural operations.

The following phosphate treatments were given over a uniform treatment of 40 lbs. of nitrogen to all the plots:

Treatment—1. No P_2O_5

2. 10 lbs. P_2O_5 per acre as superphosphate.

3. 20 lbs. P_2O_5 ,,

4. 40 lbs. P_2O_5 ,,

5. 80 lbs. P_2O_5 ,,

6. 160 lbs. P_2O_5 ,,

The treatments were replicated four times by randomization and repeated successively over six seasons. The yield of crop from each of the trials and their composition are set out in Tables 1 and 2.

TABLE No. I

Yields of Ragi grain and straw in the Experiments.

Treatments.	Summer 1952		Monsoon 1952		Summer 1953		Monsoon 1953		Summer 1954		Monsoon 1954	
	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw	Grain	Straw
1	175·5	377·5	184·0	359·0	209·0	370·0	295·0	558·0	269·0	550·0	254·0	337·5
2	188·0	377·5	246·5	520·0	222·0	410·0	327·0	583·0	302·0	565·5	282·5	350·0
3	190·5	365·0	283·0	597·5	252·0	478·o	345·o	638·0	330·0	662·5	323·5	412·5
4	205·0	362·5	299·0	619·0	267·0	513·0	333·0	657·0	372·0	702·5	331·0	430·0
5	204·0	410·0	307·0	625·0	300·0	589·0	371·0	689·0	382·0	725·0	352·0	442·5
6	211·0	375·0	324·0	629·0	306·0	594·0	387·0	704·0	392·0	779·0	375·0	457·5
Critical difference	n. s.	...	45·8	...	38·0	76·0	32·6	75·0	47·7	...	56·5	...

(Yields of grain and straw are per Sq. Yd. and average of 4 replications and are given in grams.)

TABLE No. II

Composition of the crop in the several experiments—Percentage on oven dry basis.

Treat-ments	Summer 1952				Monsoon 1952				Summer 1953				Monsoon 1953				Summer 1954			
	Grain		Straw		Grain		Straw		Grain		Straw		Grain		Straw		Grain		Straw	
	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N	P$_2$O$_5$	N
1	0·654	1·24	0·33	0·52	0·64	1·63	0·36	0·36	0·63	1·40	0·31	0·46	0·61	1·54	0·24	0·53	0·69	0·96	0·45	0·45
2	0·697	1·22	0·32	0·53	0·64	1·59	0·24	0·45	0·61	1·41	0·29	0·43	0·65	1·51	0·19	0·50	0·71	1·06	0·39	0·43
3	0·708	0·95·	0·31	0·51	0·65	1·60	0·25	0·39	0·62	1·43	0·30	0·47	0·67	1·50	0·23	0·54	0·67	0·96	0·35	0·54
4	0·668	1·02	0·33	0·59	0·66	1·63	0·28	0·38	0·65	1·40	0·30	0·45	0·65	1·55	0·29	0·51	0·64	0·96	0·30	0·60
5	0·667	1·22	0·66	0·59	0·64	1·67	0·32	0·38	0·63	1·40	0·50	0·49	0·66	1·51	0·33	0·57	0·62	0·96	0·38	0·50
6	0·705	1·24	0·52	0·57	0·63	1·71	0·36	0·37	0·67	1·46	0·51	0·51	0·68	1·50	0·42	0·49	0·66	0·93	0·43	0·59

TABLE No. III

Amount of N and P$_2$O$_5$ in gms, removed in the crop from an area of 1 Sq. Yd.

Treatments	Summer 1952				Monsoon 1952				Summer 1953				Monsoon 1953				Summer 1954			
	P$_2$O$_5$ uptake	P$_2$O$_5$ Increase over Treatment 1	N uptake	N uptake-Increase over 1	P$_2$O$_5$	Increase over 1	N	Increase over 1	P$_2$O$_5$	Increase over 1	N	Increase over 1	P$_2$O$_5$	Increase over 1	N	Increase over 1	P$_2$O$_5$	Increase over 1	N	Increase over 1
1	1·89	...	4·38	...	1·99	...	4·32	...	2·45	...	4·62	...	3·05	...	5·87	...	4·331	...	5·057	...
2	1·90	0·01	5·16	0·78	2·82	0·83	6·27	1·95	2·55	0·10	4·90	0·27	3·24	0·19	5·86	0·08	4·430	0·099	5·558	0·501
3	2·17	0·28	4·77	0·39	3·35	1·34	6·88	2·56	3·00	0·55	5·86	1·23	3·78	0·74	6·64	0·77	4·532	0·202	6·748	1·691
4	2·00	0·11	5·35	0·93	3·69	1·70	7·21	2·89	3·50	1·04	5·05	0·43	4·21	1·16	7·39	1·42	4·490	0·159	7·789	2·732
5	2·60	0·71	5·61	1·23	3·94	1·94	7·48	3·15	4·78	2·33	7·00	2·41	4·72	1·67	7·87	2·01	5·123	0·793	7·292	2·235
6	3·19	1·30	6·12	1·74	4·27	2·28	7·88	3·56	5·10	2·65	7·49	2·86	5·59	2·54	8·72	2·85	5·937	1·607	8·252	3·195

(10 lbs. of P$_2$O$_5$ and 40 lbs. N per acre are equivalent to 0·938 gms. of P$_2$O$_5$ and 3·752 gms. of N per Sq. Yd.)

The uptake of N and P_2O_5 by the crops are recorded in Table III and the increase in the uptake of these nutrients in the different treatments are also worked out.

It is seen from the data (Table I) that there is a steady increase in the yields of grain and straw in all the treatments with increasing levels of P_2O_5; these increases being significant at the 20 and 40 lbs. levels. The increase in crop yields at the 80 and 160 lbs levels are not in keeping with the large increase in the dosage of P_2O_5. The composition of the crop, Table II does not show any marked variations except for a tendency towards increase in the phosphoric acid content of straw at the higher P_2O_5 levels. Possibly the increased absorption of phosphates by the grain reaches a maximum level rapidly and the subsequent intake is accumulated only in the straw. Comparison of total intake of N and P_2O_5 by the crop (Table III) shows that the recovery of N steadily increases with increasing P_2O_5 levels and reaches its maximum at the 160 lbs. level, though the dosage of nitrogen applied is constant in all the treatments. Hence phosphate application appears to favourably influence nitrogen utilization. This is in agreement with the findings of Sircar and Sen[5] who worked with wheat. The uptake of phosphorus by the crop also increases with increasing phosphate applications, there being a 100 per cent increase at the highest phosphate level compared with the no phosphate treatment

Soil Studies—Samples of the soil were collected and composited from each of the treatments at the three depths 0-6"; 6-9" and 9-12". The analytical data relating to the total and citric acid soluble P_2O_5 of the samples collected at the beginning of the trials and at the end of 6 seasons are recorded in Table IV and V.

The ratio of the citric acid soluble to the total phosphoric acid have been worked out in each of the above samples and the same are set out in Table VI.

It is seen that both the total and the citric acid soluble phosphoric acid contents of the soil have increased and that the ratio of the citric soluble to the total phosphoric acid in the top six inches has doubled after addition of 40 lbs. P_2O_5 per acre for a period of six seasons. This ratio is not materially affected with increase in the dosage of phosphates to the 80 and 160 lbs. per acre levels.

TABLE No. IV

Total P_2O_5 content of soil at start and after six seasons—Expressed as mgs per 100 gm. of soil.

Start ... February 1952

End ... January 1955

Depths		Treatments					
		1	2	3	4	5	6
0 - 6"	At start	53·0	50 4	62·0	53·0	54·3	76·0
	At end	54·0	62·0	66·3	83·8	93·0	152·9
6 – 9"	At start	44·0	51·4	49·0	44·0	47·0	53·0
	At end	55·0	54·0	59·1	58·6	86·0	102·1
9 – 12"	At Start	33·0	51·4	39·0	38·0	37·0	43·0
	At end	39·0	42·0	40·0	41·2	40·2	53·2

TABLE No. V

Citric soluble P_2O_5 in mgs. per 100 gm. of soil.

Depths		1	2	3	4	5	6
0 – 6″	At Start	13·7	12·8	15·0	19·0	20·0	19·2
	At end	14·3	19·9	24·8	40·5	48·1	75·4
6 – 9″	At Start	12·2	12·0	10·5	11·0	17·6	14·5
	At end	13·5	15·2	20·7	28·1	35·2	42·8
9 – 12″	At Start	7·2	11·0	5·5	8·4	11·3	8·4
	At end	9·6	13·9	8·5	18·2	21·1	19·8

TABLE No. VI

Ratio of C. S. P_2O_5 to Total P_2O_5—Expressed as percentage.

Depths		1	2	3	4	5	6
0 – 6″	At Start	26·0	23·0	24·2	35·8	37·0	25·3
	At end	26·5	32·2	37·4	48·3	51·7	49·3
6 – 9″	At Start	27·5	23·3	21·4	25·0	37·6	27·4
	At end	27·0	28·1	35·0	39·4	40·9	41·9
9 – 12″	At Start	21·8	21·4	14·1	21·6	30·5	19·5
	At end	24·6	33·1	21·3	44·2	50·2	37·2

Further the phosphates present in the 6 to 9 and 9 to 12 inch depths indicate that the penetration by the added phosphate is rapidly retarded, but the ratio of the citric soluble to the total phosphate appears to be kept up at the same level as in the surface layers indicating presence of larger proportions of these available forms in these layers. This is noticeable with the 40 lbs. per acre and higher levels of P_2O_5. These data therefore indicate that the maximum advantages of maintaining the highest level of Citric acid soluble P_2O_5 can be achieved by fertilizing at the 40 lbs. P_2O_5 per acre level and that increasing this dosage further does not result in any benefit.

SUMMARY

Increasing doses of phosphoric acid from 0 to 160 lbs. P_2O_5 per acre were applied to a red sandy loam in six successive seasons and the influence of these applications on the crop yield, uptake of nitrogen and phosphoric acid by the crop and distribution of the citric soluble and total phosphoric acid in the soil studied. Increases in the yield of Ragi, the crop studied here, are significant upto the 40 lbs P_2O_5 per acre levels, while further increases do not show response in crop yield. The total uptake of nitrogen by the crop appears to be influenced by the phosphate applications, while the total phosphate uptake also increases with increasing phosphate applications, this being largely due to uptake by the straw of the crop. The phosphate distribution in the soil indicates that application of 40 lbs. P_2O_5 per acre doubles the citric soluble constituent originally present in the soil and that increases in phospate application do not increases this to any large extent.

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EFFECT OF PHOSPHORIC ACID ON LEACHING OF LIME

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No method of improving the soil other than fertilizing or cultivating it is so important as liming or chalking. Sir John Russell writing in the Journal of Agriculture, states : "Of all the soil constituents none is so seriously liable to loss as lime." Lime an essential plant food, is removed from the soil by crops grown there on, but the percentage of lime found in average crops is so small that the loss from the soil in this direction is not very marked. On the other hand, however, the loss of lime by actual drainage from the soil is very considerable and may amount to several hundred pounds of lime per acre yearly.

When at any time the amount of rainfall entering a soil becomes greater than its water-holding capacity, losses by leaching tend to occur. Water percolating through the soil becomes charged with CO_2 gas and is capable of dissolving the calcium carbonate from the soil as $Ca(HCO_3)_2$. Lime is also lost as nitrate produced either from the nitrification of proteins or fertilizer addition. The losses of lime are recorded from $\frac{1}{4}$ to $\frac{1}{2}$ ton of lime per acre per annum.

A large amount of work on the leaching of plant food materials by drainage has been carried on in different parts of the world. Some of the results obtained regarding the losses of lime at Rothamsted, Aberdeen, New York State, Florida, are 330, 76, 267 and 140 lbs. per acre per annum respectively. Ten year results from Cornell University lysimeters reported by Bizzell and Lyon[1], show an annual loss of 995 lbs. of $CaCO_3$ per acre from the bare soil and 535 lbs. from plots that grew crops. In North Central States of the U.S.A. the loss of lime ranges between 100-500 lbs. per acre.

In this laboratory intensive work is being carried on for the last few years on the influence of phosphates in saving the washing of lime from soils and it has been proved experimentally as well as theoretically that the presence of phosphates in soils hinders markedly the loss of lime. Dhar[2] has stated that the addition of calcium phosphate to the soil is better than adding calcium carbonate to the soils as phosphate decreases the washing away of lime from soils. Misra[3] has shown that the loss of lime from soils rich in phosphates is less than in soils poor in phosphate. MacIntire and Shaw[4] have shown by lysimeter experiments that by applying 1000 lbs. of K_3PO_4 per acre about 636 lbs. of $CaCO_3$ are saved in a period of 8 years.

We have carried on experiments to find out the effect of phosphoric acid on the leaching of lime from soils.

EXPERIMENTAL PROCEDURE

10 gms. of a soil of known composition were taken in different glass stoppered bottles and 100 c.c. of phosphoric acid of different concentrations were added. The bottles were shaken vigorously for one hour and left for 24 hours. The

solutions were filtered off by means of a Buchner funnel. The filtrates were analysed for their calcium contents and the residues were carefully transferred to the bottles with distilled water and the volume of 1 liquid in each bottle was made upto 100 c.c. by distilled water. The bottles were again shaken vigorously and left for 24 hours. Next day the solutions were again filtered off and the filtrates were analysed for calcium contents and the residues were again transferred to the bottles. The volumes were made upto 100 c.c. by distilled water and the whole process was repeated for seven times in order to obtain seven washings of the soil.

The same experiments were also carried out first by adding 1% Ca as calcium silicate and 1% Ca as calcium carbonate to the soil and to the bottles 100 c.c. of different concentrations of phosphoric acid were added. The filtrates in each case were analysed for their calcium contents.

<div align="center">

RESULTS

TABLE No. 1

Analysis of the soil.

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Loss on ignition	... ...	3·018%
HCl insoluble	... ...	78·474%
Sesquioxide	... ...	10·06 %
Fe_2O_3	... ...	4·504%
Total P_2O_5	... ...	0·13 %
1% citric acid soluble P_2O_5	...	0·0287%
CaO	... ...	2·625%
MgO	... ...	1·952%

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TABLE No. 2.

Soil + Phosphoric acid.

Calcium given out as calcium oxide per 100 gms. of the soil.

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P₂O₅ applied in lbs. per acre.	15904	3180·8	1590·4	318·1	159·4	31·8	15·9
No. of washings	No.P₂O₅ (100 c.c. water alone) mgm.	M/100 mgm.	M/500 mgm.	M/1000 mgm.	M/5× 10³ mgm.	M/10× 10³ mgm.	M/50× 10³ mgm.	M/100× 10³ mgm.
1	28·36	238·00	69·38	52·22	27·60	23·86	23·12	21·62
2	17·90	66·40	31·32	26·10	16·41	14·17	14·17	12·68
3	14·17	33·56	23·12	15·29	14·17	14·17	14·92	13·43
4	14·91	23·12	24·62	19·40	14·92	16·41	15·29	14·17
5	11·92	19·39	14·92	14·17	13·43	12·68	11·93	10·44
6	14·17	15·29	16·41	12·68	14·17	12·68	11·94	14·17
7	17·15	17·15	17·90	14·92	17·90	16·41	17·16	17·16
Total loss...	118·58	412·91	197·67	154·78	118·60	110·38	108·53	103·67
Loss in lbs. per acre.	2656	9249	4427	3467	2656	2472	2430	2322

<div align="center">[377]</div>

TÀBLE No. 3.

Soil + Phosphoric acid + 1% Ca as CaSiO$_3$

Calcium given out as calcium oxide in mgms. per 100 gms. of the soil

1	19·04	200·70	63·84	39·20	22·40	19·04	16·80	14·55
2	15·68	84·16	31·36	22·40	17·90	14·55	15·68	14·55
3	20·16	41·44	21·28	16·80	14·55	14·55	13·44	13·44
4	15·68	30·24	16·80	19·04	19·04	19·04	17·92	15·68
5	14·55	16·80	14·55	13·44	15·68	15·68	14·55	13·44
6	13·44	14·55	13·44	13·44	11·20	12·32	12·32	13·44
7	14·55	15·68	13·44	13·44	11·20	11·20	11·20	13·44
Total loss...	113·1	403·57	174·71	137·76	111·99	106·38	101·91	98·54
Loss in lbs. per acre.	2533	9039	3913	3085	2508	2382	2282	2207

TABLE No. 4

Soil + Phosphoric acid + 1% Ca as CaCO$_3$

Calcium given out as calcium oxide in mgms. per 100 gms. of the soil.

P$_2$O$_5$ applied in lbs. per acre		1590·4	3180·8	1590·4	318·1	159·0	31·8	15·9
No. of washings	No phosphoric acid Soil + water	M/100	M/500	M/1000	M/5 × 10^3	M/10 × 10^3	M/50 × 10^3	M/100 × 10^3
		mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	21·28	179·20	58·26	39·20	25·75	20·16	19·04	12·32
2	16·80	56·01	28·00	23·52	16·80	13·44	11·20	12·32
3	14·55	35·83	19·04	15·68	15·68	14·55	12·32	10·08
4	16·80	31·36	15·68	14·55	14·55	14·55	14·55	14·55
5	14·55	30·24	17·92	15·68	13·44	12·32	12·32	12·32
6	14·55	25·75	14·55	13·44	10·08	13·44	14·55	16·80
7	13·44	22·40	12·32	13·44	12·32	13·44	14·55	14·55
Total loss	111·97	380·79	165·77	135·51	108·62	101·90	98·53	92·94
Loss in lbs. per acre.	2508	8529	3713	3035	2433	2282	2207	2081

|	No phosphoric acid Soil+water	M/100	M/500	M/1000	M/5×10³	M/10×10³	M/50×10³	M/100×10³
Loss of lime by the soil in lbs./acre	2656	9249	4427	3467	2656	2472	2430	2322
Saving of lime in lbs./acre by H_3PO_4		(−)6593	(−)1771	(−)811	Nil	(+)184	(+)226	(+)334
Loss of lime by $CaSiO_3$+soil in lbs./acre	2533	9039	3913	3035	2508	2382	2282	2207
Saving of lime in lbs./acre by $CaSiO_3$ and H_3PO_4		(−)6506	(−)1380	(−)552	(+)25	(+)151	(+)251	(+)326
Saving of lime by $CaSiO_3$ alone.		(+)87	(+)391	(+)259	(+)25	(−)33	(+)25	(+)8
Loss of lime by soil $CaCO_3$ in lbs./acre.	2508	8529	3713	3035	2433	2282	2207	2081
Saving of lime in lbs./acre by $CaCO_3$ and H_3PO_4		(−)6021	(−)1205	(−)527	(+)65	(+)226	(+)301	(+)427
Saving of lime by $CaCO_3$ alone.		(+)572	(+)566	(+)284	(+)65	(+)42	(+)75	(+)113

DISCUSSION

The experiments on the leaching of lime clearly show that a considerable amount of lime is lost when the soils are washed with distilled water. The addition of phosphates to soils leads to the preservation of $CaCO_3$ chiefly because in normal soils $CaHPO_4$ is readily formed when the soil is rich in calcium carbonate and to which a phosphate is added. Moreover, the solubility of $CaHPO_4$ is much less than that of $Ca(HCO_3)_2$ which is also formed in the soil especially in the presence of decomposing organic matter.

The dissociation constants of H_2CO_3 and H_3PO_4 are as follows :—

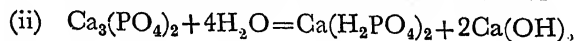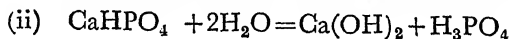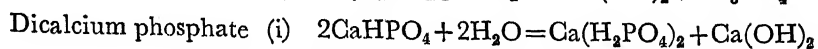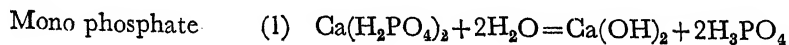| Acid	Dissociation constant	First dissociation constant	Second dissociation constant	Third dissociation constant
Carbonic acid	3×10^{-7}	3×10^{-7}	6×10^{-11}	
Phosphoric acid	9×10^{-3}	$1 \cdot 1 \times 10^{-2}$	2×10^{-7}	$3 \cdot 6 \times 10^{-13}$

It appears, therefore, from the above table that the third dissociation constant of phosphoric acid is much smaller than the second dissociation constant of carbonic acid. Hence when H^+ ions come in contact with the phosphate ions in the soil, HPO_4 ions are formed more readily than HCO_3' ions by the action of carbonate ions on hydrogen ions. Moreover, $CaHPO_4$ is much less soluble than $Ca(HCO_3)_2$ and thus the lime status of the soil is preserved.

From table No. 2 it is clear that small doses of phosphoric acid help in the saving of lime of the soil but large amounts cause more leaching. The large amounts of phosphoric acid applied, react with the $CaCO_3$ of the soil and form $Ca(H_2PO_4)_2$, while the small amounts of H_3PO_4 form $CaHPO_4$ as it is clear from the following equations :—

1. $CaCO_3 + 2H_3PO_4 = Ca(H_2PO_4)_2 + H_2CO_3$

2. $CaCO_3 + H_3PO_4 = CaHPO_4 + H_2CO_3$
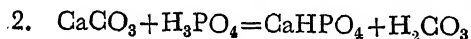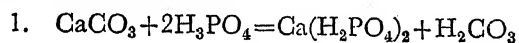
Two moles of phosphoric acid react with $CaCO_3$ and form a readily soluble compound $Ca(H_2PO_4)_2$ (4·0 parts soluble in 100 parts of water at 15°C) while only one mole of phosphoric acid forms a very slightly soluble compound $CaHPO_4$ (0·028 parts soluble in 100 parts of water at O°C), therefore, the losses of lime by the application of large amounts of H_3PO_4 are greater.

From table No. 5 it is also clear that the addition of $CaSiO_3$ and $CaCO_3$ to the soil, saves the loss of lime by leaching. Phosphates of calcium (mono, di, tri calcium phosphates) formed by the addition of phosphoric acid hydrolyse as follows :—

Mono phosphate   (1) $Ca(H_2PO_4)_2 + 2H_2O = Ca(OH)_2 + 2H_3PO_4$

Dicalcium phosphate (i) $2CaHPO_4 + 2H_2O = Ca(H_2PO_4)_2 + Ca(OH)_2$

               (ii) $CaHPO_4 + 2H_2O = Ca(OH)_2 + H_3PO_4$

Tricalcium phosphate (i) $Ca_3(PO_4)_2 + 2H_2O = 2CaHPO_4 + Ca(OH)_2$

               (ii) $Ca_3(PO_4)_2 + 4H_2O = Ca(H_2PO_4)_2 + 2Ca(OH)_2$

               (iii) $Ca_3(PO_4)_2 + 6H_2O = 3Ca(OH)_2 + 3H_3PO_4$
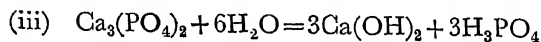
Thus by hydrolysis, less soluble phosphates are converted into more soluble forms and lime. By the addition of $CaSiO_3$ and $CaCO_3$, which are both alkaline there is a checking of the hydrolysis. Hence the losses of lime by the addition of $CaCO_3$ or $CaSiO_3$ are reduced.

SUMMARY

1. Application of pbosphoric acid in small doses helps in the saving of lime to a considerable extent while large doses, inspite of saving the lime increase the loss of lime from soils. Hence the application of small amounts of phosphates are more useful.

2. Calcium carbonate and calcium silicate check the hydrolysis of phosphates formed by the addition of phosphoric acid to the soil. Due to the checking of hydrolysis the losses of lime are diminished.

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THE ROLE OF PHOSPHATE IN GLYCOLYSIS AND SYNTHESIS OF POLY- AND DI-SACCHARIDES IN GREEN GRAM

(Phaseolus radiatus)

By

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INTRODUCTION

Although the key role of phosphate in the development and growth of plant life has been recognised from a long time only during the past few years the significance of the phosphorylated intermediates in the metabolic processes has been understood. Much of the work has been stimulated by the identification of phosphorylated sugar intermediates in the phosphorolysis of starch by plant extracts. The pioneering investigations of Tanko[1], James [2,3,4] and Hanes [5] have led to the belief that essentially the same mechanisms as those in animal and yeast might be operating in plants as well. This has led to a tendency to duplicate the results obtained in animal and yeast metabolism in plant tissues and the considerable amount of literature accumulated reveals that the systems involved in the transformation of sugars are strikingly similar to those found in animal and yeast sources and the subject has been excellently reviewed by Stumpf[6,7]. We do not wish to summarise all the existing information in the field, in this review, but we will restrict ourselves in emphasising the data obtained in our laboratory on the glycolytic and poly— and di-saccharide synthesising enzymes in green gram (Phaseolus radiatus).

The scheme presented below outlines the present status of breakdown of the carbohydrates in green gram. To facilitate discussion, the subject is divided into the following sections: 1. Formation of starch; 2. Interconversion of hexose phosphates; 3. Hexose monophosphate shunt, 5. Transformation of Triose phosphates; and 5. Sucrose problem.

FORMATION OF STARCH

Amylose→Amylopectin (Q-enzyme).

Glucose-1-Phosphate ⇌ Amylose + Phosphate (Phosphorylase).

During the past few years considerable information has become available concerning the synthesis of amylose and amylopectin, the two components of starch, by enzyme systems isolated from plant tissues. Ever since the discovery by Hanes[5] of the existence of phosphorylase in potato and peas, which synthesises amylose from G-1-P, the isolation and characterisation of the other enzyme responsible for the synthesis of amylopectin from amylose in plants has been the subject of intensive study by Peat and co-workers[8]. The two enzymes were identified in the water extracts of powder of green gram seeds and they have been purified to some extent by ammonium sulfate fractionation by Sri Ram and Giri [9]. Some of the properties

of these enzymes have been studied which include the inhibition of phosphorylase by salivary α-amylase, β-amylase of sweet potato and soyabean, and aqueous extracts of wheat and barley. The primer specificity of the enzyme has also been investigated by Giri and Saroja[10].

Phosphorylase preparations have been obtained from the following plants: peas[5], waxy maize[11], sweet corn[12], barley[13], broad beans[14], lima bean[15], jack bean[16], sweet potato[17], sugar beet[18], squash[19], pumpkin[20], and potato[21,22]. In our laboratory, it was observed[23], that phosphorylase occurs in many of the pulses while it could not be detected in cereals.

INTERCONVERSION OF HEXOSE PHOSPHATES
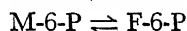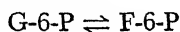
Phosphoglucomutase

G-1-P $\rightleftharpoons$ G-6-P
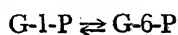
Phosphoglucomutase, the enzyme which converts G-1-P to G-6-P has been shown to be present in green gram seed extracts and partially purified by ammonium sulfate fractionation by Ramasarma, Sri Ram and Giri [24]. The enzyme has been found to be activated by Mg^{++}, Mn^{++} and Co^{++}. Metal binding agents such as cysteine do not activate the enzyme. Among the several inhibitors for the enzyme are, Na^+, Hg^{++}, Ag^+, Cu^{++}, and KCN. The properties of the enzyme have also been studied. Added coenzyme, glucose diphosphate, activates the enzyme, although the substrate used was associated with the necessary catalytic amounts of the coenzyme.

The enzyme has been reported in the following plants: peas[5], tomato leaf plastids[25], jack bean seeds[26] and broad bean[27].

Hexokinase: Green gram seed extracts were able to phosphorylate hexose sugars, glucose, galactose, mannose and fructose in the presence of ATP and the ability of phosphorylation decreases in the order given above. Mitochondria and supernatant preparation of green gram seedlings have been shown to exhibit similar properties by Giri, Ramasarma and Nagabhushanam[28].

Stafford, Barnett, Conn and Vennesland[29], reported phosphorylation of glucose, fructose, mannose and galactose by wheat germ enzyme and Saltman studied the glucose phosphorylating enzyme in potato tubers, mung bean hypocotyls, sweet potato root, pine pollen, cauliflower inflorescence and wheat germ[30].

Phosphohexose Isomerase :

G-6-P $\rightleftharpoons$ F-6-P

M-6-P $\rightleftharpoons$ F-6-P

The two isomerases convert G-6-P and M-6-P into F-6-P and they are named phosphoglucose isomerase and phosphomannose isomerase[31]. We have identified phosphoglucose isomerase (G-6-P $\rightleftharpoons$ F-6-P) in green gram seed extracts and partially purified it by acetone fractionation[32]. The enzyme has been found to be very stable in alkaline condition. It is rapidly inactivated when heated above 45° in acid pH range. Equilibrium is approached rapidly at which 60% of G-6-P and 40% of F-6-P are found to exist. No metal activation or cofactor are found. The enzyme has been found to be distributed in every part of the plant, root, stem and leaves.

The enzyme was found in peas[33] and was assumed to be wide spread in all tissues.

Phosphofructokinase :

$$F6P + ATP \rightleftharpoons FDP + ADP$$
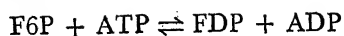
In presence of ATP, F-6-P has been found to be phosphorylated by green gram extracts. The reaction was followed manometrically according to the method of Muntz[35].

Considerable information is available on this enzyme in pea seeds [36]. The enzyme was found in oat seeds, sunflower fruit, tomato seed, pondersa pine pollen, leaf and seed of pea, and seeds of radish, soyabean, broad bean and corn.
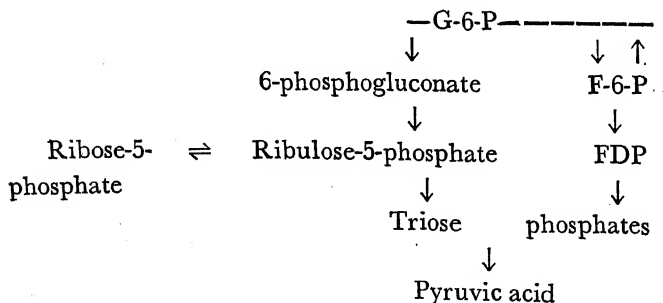
Aldolase :

$$FDP \rightleftharpoons \text{3-phosphoglyceraldehyde} + \text{Dihydroxyacetone phosphate}$$
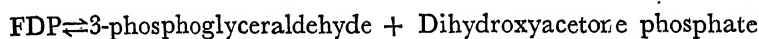
Aldolase activity has been identified in green gram seed extracts [34] by fixing triose phosphates with sodium bisulfite and estimating them as alkali-labile phosphorus according to the method of Herbert, Gordon, Subrahmanyan and Green[37]. The enzyme was partially purified by ammonium sulfate fractionation. Several of the properties of this enzyme in green gram were studied. Even the ammonium sulfate fractionated enzyme showed considerable fructose diphosphatase activity reported by Gomori[38], which was however inhibited by the bisulfite.

Stumpf [39] isolated and studied the properties of pea aldolase. Tewfik and Stumpf [40] found that the distribution of aldolase in plants to be ubiquitous. Twenty nine species ranging through fungi, ferns, conifers, monocotyledons, and dicotyledons have been shown to contain aldolase.

HEXOSEMONOPHOSPHATE SHUNT

Warburg[41] demonstrated in 1936 that G-6-P can be degraded by a pathway other than glycolysis. In presence of TPN, G-6-P can be oxidised to 6-phosphogluconic acid. Dickens[42] demonstrated the accumulation of pentose, which was believed to be the main product of the oxidative degradation of G-6-P. Investigations of Horecker with yeast[43], Cohen with yeast and bacteria[44] and Dickens with animal extracts[45] suggest the following shunt mechanism :

$$
\begin{array}{ccc}
\text{—G-6-P} & \text{—} & \text{—} \\
\downarrow & & \downarrow \uparrow \\
\text{6-phosphogluconate} & & \text{F-6-P} \\
\downarrow & & \downarrow \\
\text{Ribose-5-} \rightleftharpoons \text{Ribulose-5-phosphate} & & \text{FDP} \\
\text{phosphate} & \downarrow & \downarrow \\
& \text{Triose} & \text{phosphates} \\
& \downarrow & \\
& \text{Pyruvic acid} &
\end{array}
$$

Conn and Vennesland[46] suggested that such a shunt mechanism was operating in plants and they demonstrated the presence of G-6-P dehydrogenase in several

plant extracts. The recent work of Axelrod and Bandurski [47] fully documented the evidence for the presence of the shunt mechanism in extracts of acetone powder of spinach leaf.

Green gram extracts showed G-6-P-dehydrogenase activity[34]. Partially dialysed extracts were added to G-6-P and TPN and the absorption of the reduced TPN was followed by spectrophotometer. The reduction in the absence of the substrate was negligible. Pentose was formed in the reaction mixture measured according to the orcinol method of Meijbaum.

Preliminary experiments showed that ribose-5-phosphate was isomerised to ribulose-5-phosphate by green gram extracts. Also the green gram extracts were capable of breaking ribose-5-phosphate further which was followed by the reduction in the pentose and increase in the triose phosphates. Further work will be taken up to elucidate this pathway in green gram.

TRANSFORMATIONS OF TRIOSES

Aldolase breaks the hexose molecule into two triose phosphates and these trioses further metabolised to give pyruvic acid, and this involves several enzyme systems bringing about transformations in triose phosphates. Indication for the presence of this system in green gram extracts was gathered by designing an experiment to follow the breakdown of FDP to phosphoglyceric acid manometrically on the lines of Stumpf[48]. When FDP and green gram extract were incubated, the aldolase present splits up FDP into glyceraldehyde and dihydroxyacetone phosphates. The glyceraldehyde phosphate is oxidized in presence of DPN and arsenate to Diphosphoglyceric acid which breaks down to 3-PGA. The acid produced liberated carbon dioxide from the bicarbonate when fluoride was added to inhibit the enolase action. The DPN can be oxidised if acetaldehyde was introduced into the reaction mixture thus affecting the complete breakdown of FDP into 3-PGA, the acetaldehyde being reduced to alcohol by alcohol dehydrogenase. Without added Arsenate, acetaldehyde and DPN there will be little evolution of gas while in the complete system there will be two equivalents amount of liberation of carbon dioxide for one equivalent of FDP. Aldolase, triose phosphate isomerase, triose phosphate dehydrogenase, and alcohol dehydrogense have been indicated to be operating in green gram extracts by the above mentioned experiment. Further tests to identify these enzymes have also been done and they are enumerated below.

### Triose phosphate isomerase :

The breakdown of FDP produces two equivalents of acid, which could not have been realised if the two triose phosphates are not equilibrated by the isomerase, since, of the two triose phosphates cleaved from FDP only phosphoglyceraldehyde is oxidised by the dehydrogenase. The other triose phosphate, dihydroxy-acetone phosphate would have accumulated, if it were not in equilibrium with phosphogleceraldhyde, as it is not attacked by the dehydogenase. No further test was done to confirm the presence of this enzyme.

Triose phosphate dehydrogenase :

3-phosphoglyceraldehyde + DPN + phosphate $\rightleftharpoons$ 1,3 Diphosphoglyceric acid + $DPNH_2$
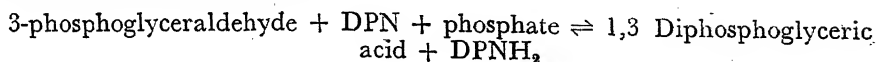
The presence of this enzyme has been confirmed by following the absorption of the reduced DPN in spectrophotometer using a dialysed extract as the source for both aldolase and the dehydrogenase and FDP as the substrate.

[385]

Phosphoglyceryl kinase :

$$ADP + 1,3\text{-Diphosphoglyceric acid} \rightleftharpoons ATP + 3\text{-phosphoglyceric acid}$$
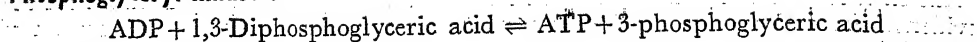
The reaction has been studied in green gram by the Lipmann-Tuttle hydroxamine method. Phosphoglycerate and ATP in presence of green gram extract to form diphosphoglycerate and the diphosphoglycerate combined with hydroxylamine and gave purple colour on addition of $FeCl_3$.

Using this technique this enzyme has been studied in detail in pea seed[49] and tomato, *Byrophyllum*, *Silene*, *Xanthium*, potato tuber, sweet potato, mung bean, soyabean, corn seed and wheat germ.

Phosphoglyceromutase :

$$3 - PGA \rightleftharpoons 2 - PGA$$
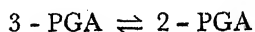
Phosphoglyceromutase has been demonstrated in peas by Stumpf [48] indirectly. In presence of Mg^{++} and ADP, $3 - PGA$ is converted into pyruvic acid by pea seedling extracts by the combined action of phosphoglyceromutase, Enolase and Phosphoglyceryl kinase. We have now been able to demonstrate the enzyme directly by the polarimetric method of estimation of the $3 - PGA$ formed from $2 - PGA$ according to Sutherland *et al*[50]. Fluoride was added to inhibit the enolase action. Green gram extracts were active without the addition of the coenzyme, 2,3—diphosphoglyceric acid, which was probably present in the extracts.

Enolase :

$$2 - PGA \rightleftharpoons \text{Phosphoenolpyruvic acid} + H_2O$$
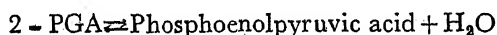
Phosphoenolpyruvic acid liberates phosphorus on treatment with iodine. Enolase was identified by the increase in iodine labile phosphorus on incubation of either $3 - PGA$ or $2 - PGA$ with green gram extracts. It was observed that initially there was an increase in iodine-labile phosphours but decreased on longer incubation simultaneously giving rise to inorganic phosphorus and pyruvic acid. Addition of fluoride inhibits the formation of iodine-labile phosphorus as well as pyruvic acid completely while the liberation of inorganic phosphorus was inhibited partially. Phosphoenolpyruvic acid does not give colour with Friedman-Haugen reagent used for the estimation of pyruvic acid. Since pyruvic acid is formed in the reaction mixture, it must have come from the phosphoenolpyruvic acid by dephosphorylation which view is substantiated by the observed increase in inorganic phosphorus that always accompanied formation of pyruvic acid. It was not, however, clear whether the phosphoglyceric acids also were dephosphorylated or not. The activation of enolase by Mg^{++} could not be valuated as measured by the increase in iodine-labile phosphorus, because of the fact the phosphatase was also activated and more of inorganic phosphorus and pyruvic acid were formed. But it is evident that the enolase must have been activated to be able to supply more of the phosphoenolpyruvic acid for the phosphatase to produce more pyruvic acid. The combined amounts of iodine-labile phosphorus and pyruvic acid should be taken as the measure of the enolase activity.

Phosphopyruvic kinase :

$$\text{Phosphoenolypyruvic acid} + ADP \rightleftharpoons \text{Pyruvic acid} + ATP.$$
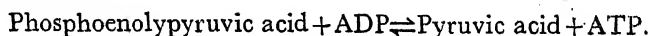
This enzyme system has been identified in green gram extracts by determining the amount of pyruvic acid formed from $2 - PGA$ in presence and absence of ADP. As has been pointed out above some pyruvic acid was formed by phosphatase action ; but in presence of added ADP a large excess of pyruvic acid was formed which was taken as the measure of the kinase activity.

The alternate pathway of producing pyruvic acid from phosphoenolpyruvic acid without the mediation of ADP was an interesting feature in green gram. Phosphopyruvic kinase transfers a high energy phosphate bond from phosphoenolypyruvic acid to ADP. The significance of hydrolysis of the phosphoenolpyruvic acid by phosphatase involving a wastage of the energy of the phosphate bond will be understood only after more detailed work on the subject is carried out. This enzyme system has been identfied in pea seed[48].

Carboxylase :

$$\text{Pyruvic acid} \rightarrow \text{Acetaldehyde} + CO_2.$$
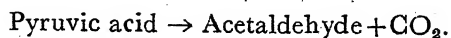
Green gram extracts decarboxylated pyruvic acid to acetaldehyde and carbon dioxide. Mg^{++} activated the enzyme. Addition of cocarboxylase was not necessary for the enzyme action which was probably present in the extract. Further work was not carried out since the enzyme was clearly defined by Vennesland and Felsher[51] in many plants including several legumes.

THE SUCROSE PROBLEM

One of the most intriguing problems in plant biochemistry is the elucidation of the mechanism of sucrose synthesis. Sucrose phosphorylase investigated by Doudoroff, Hassid and Barker[52] in *Pseudomonas saccharophila* could not be identified in plants except for the recent reports of Turner[53, 54] on its presence in pea seed extracts. More recently Gardini, Leloir and Chiribogo[55] reported a different type of enzyme that involves a transfer of glucose residue from uridinediphosphate glucose to fructose was concerned in the sucrose synthesis in plants. Although our attempts to isolate any enzyme system capable of synthesising sucrose were not successful, we obtained interesting results on sucrose synthesis *in vivo* on incubating sugars, sugar phosphates and other phosphorylated compounds with green gram plants. 5-10 days old plants of 2-3″ in length were incubated with the various substances by dipping the roots in 5 c. c. of solutions, in dark for 24 hours. Plants incubated with water alone decreased in their sucrose content while incubation with glucose resulted in a steady increase in sucrose. Various sugars which resulted in increasing sucrose content are : glucose, fructose, mannose, galactose, maltose and sucrose. It has been suggested by many workers[56,57,58] that glycolytic intermediates might play a significant role in sucrose synthesis, since in short term photosynthesis experiments with labelled $C^{14}O_2$, hexose phosphates were found to be labelled while the free sugars were not radioactive. Phosphorylated hexoses, G-1-P, G-6-P, F-6-P and FDP, however, did not give rise to marked increase in sucrose content. Whether or not the inability of hexose phosphates to induce sucrose synthesis depends on the permeability or not was not clear. Surprisingly the phosphorylated glyceric acids, 2-PGA and 3-PGA, which were known to be the earliest products of CO_2 fixation, proved to be very effective precursors for sucrose synthesis in green gram. β-glycerophosphate also was effective, Cyanide was known to inhibit the oxidative processes and also CO_2 fixation[59]. Sucrose synthesis in green gram was inhibited in the presence of O. OIM cyanide in the incubation medium and also in the absence of oxygen, which suggested that an oxidative system might be participating in the sucrose synthesis. Aresenite, known to uncouple phosphorylation from esterification inhibited sucrose formation suggesting there by that esterification of phosphate coupled with oxygen uptake yielding energy rich bonds might also have a significant role. Iodoacetic acid, however, showed very little inhibition of sucrose formation indicating that enzymes dependent on functional-SH groups for their activity were not involved. Calvin and others also observed that iodoaceta-

mide poisioned *Chlorella* cells did not prevent or decrease the amount of C^{14} activity in sucrose but they actually increased it 3·5 times as much. If the path of carbon from CO_2 to sucrose in photosynthesis involves reduction of 3-PGA *via* the triose phosphate dehydrogenase, the sucrose formation should be inhibited by iodoacetamide and C^{14} activity should accumulate in 3-PGA while neither of them were observed. Similarly in green gram also sucrose actually recorded an increase when incubated with iodoacetate. Fluoride facilitated the formation of sucrose in green gram plants incubated with water or glucose solution; but it inhibited markedly the formation of sucrose from 3·PGA. Although the synthesis of sucrose has been very well established *in vivo*, the precise nature of the enzyme system involved in not yet clear. It has been pointed out that more than one system might be responsible. Since phosphoglycerates have been utilised for the sucrose synthesis, it may be conjectured with some reserve, that the triose phosphates might be participating in sucrose synthesis either by combining with each other or with some other hexose phosphate[60].

The following abbreviations were used throughout the text :—

Glucose-1-phosphate = G-1-P

Glucose-6-phosphate = G-6-P

Fructose-6-phosphate = F-6-P

Mannose-6-phosphate = M-6-P

Fructose diphosphate = FDP

Diphosphopyridine nucleotide = DPN

Triphosphopyridine nucleotide = TPN

3-phosphoglyceric acid   = 3-PGA

2-phosphoglyceric acid   = 2-PGA

Adenosinetriphosphate   = ATP

Adenosindiphosphate   = ADP

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GLYCOLYTIC ENZYMES IN GREEN GRAM (*Phaseobus radialus.*)

AMYLOPECTIN

↑　　　Q-enzyme

AMYLOSE　　　　　　　　　　　GLUCOSE

　　　　　　　　　　　　　$\begin{array}{c}\text{ATP}—\\ \text{ADP}←\end{array})$ |

⇅　　Phosphorylase　　　　　　　　　↓　　Hexokinase

GLUCOSE-1-PHOSPHATE　⇌　GLUCOSE-6-PHOSPHATE

　　　　Phosphoglucomutase　　⇅　Phosphoglucose isomerase

　　　　　ATP→ADP

FRUCTOSE ————→ FRUCTOSE-6-PHOSPHATE

　　　　ADP

　　　Hexokinase　　$(\begin{array}{c}→\text{ATP}—\\ —\text{ADP}←\end{array})$　⇅　Phosphofructokinase

FRUCTOSE-PHOSPHATE+PHOSPHATE←FRUCTOSE DIPHOSPHATE

　　　　Fructose diphosphatase　　|　Aldolase

GLYCERALDEHYDE PHOSPHATE　⇌　DIHYDROXYACETONE
　　　　　　　　　　　　　　　　　　　PHOSPHATE

$(\begin{array}{c}—\text{DPN}←\\ →\text{DPNH}_2—\end{array})$　⇅　　Triose phosphate isomerase
　　　　　　　　　　　　Triosephosphate dehyrogenase

1, 3-DIPHOSPHOGLYCERIC ACID

$(\begin{array}{c}—\text{ADP}←\\ →\text{ATP}—\end{array})$　⇅　Phosphoglyceryl kinase

3-PHOSPHOGLYCERIC ACID

⇅　　Phosphoglyceromutase

2-PHOSPHOGLYCERIC ACID

⇅'　　Enolase

　　　　　　　Phosphatase
PHOSPHOENOLPYRUVIC ACID ————→ PYRUVIC ACID+PHOSPHATE

$(\begin{array}{c}—\text{ADP}←\\ →\text{ATP}-\end{array})$　⇅　Phosphopyruvic kinase

PYRUVIC ACID

↓　　　Carboxylase

ACETALDEHYDE+CO_2

$(\begin{array}{c}—\text{DPNH}_2←\\ →\text{DPN}——\end{array})$　⇅　Alcohol dehydrogenase

ALCOHOL

[390]

HYPOTHYROIDISM AND PHOSPHATE

METABOLISM IN SEMINAL VESICLES

By

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Phosphorus in organic or inorganic combinations plays many vital parts in the animal body including the metabolism of substances such as carbohydrate, fat and proteins, through what is called phosphorylating mechanism.

Many reactions with an apparent positive free energy occur in living cells, such as synthesis of all sorts, including formation of urea, proteins, polysaccharides and fats[1]. Such a reaction cannot proceed alone because only reactions with negative free energy are spontaneous. Therefore some other reaction must provide energy to drive reaction with a positive free energy. There must be some mechanism for coupling the energy-supplying (exergonic) and energy-utilizing (endergonic) reactions. Adenosine-triphosphate (ATP) is a common source of energy. It releases the energy possessed by it to endergonic reactions. ATP can act by phosphorylating a reactant; this stores sufficient energy to make the free energy change of the subsequent reaction negative when it occurs with release of phosphate.

The energy released by hydrolysis of ATP is considerably greater than the amount released by hydrolysis of phosphate esters such as glycerophosphate, ethyl phosphate, etc. The latter are termed "low-energy phosphate esters" (—ph). ATP is termed a "high-energy phosphate ester" (~ph). The two terminal phosphate bonds, the energies of hydrolysis of which are responsible for the designation "high energy", are actually acid anhydride bonds made from two phosphoric acids. Mixed anhydrides of carboxylic and phosphoric acid, such as acetyl phosphate and 1,-3-di-phosphoglyceric acid and anhydrides of phosphoric acid (Adenosine triphosphate, Adenosine - diphosphate (ADP) and various coenzymes (Co) containing pyrophosphate such as coenzyme I) are also "high-energy" compounds. The other types of ~ph compounds are found in biological systems. One type is represented by phosphocreatine (and phosphoarginine). The other is phosphoenol pyruvate. Recently compounds of coenzyme A have been found to provide extraordinarily large amount of energy. These are acetyl Co A, butyryl Co A, succinyl Co A, and Co A pyrophosphate.

Before glucose or any other monosaccharide can be utilized metabolically in any manner by the animal organism, it must be phosphorylated and enter the glycolytic cycle. It is by way of this glycolytic pathway that the major portion of the sugar enters the tricarboxylic acid or oxidative cycles of the cell.

All cells which utilize free sugars contain a group of anzymes called the hexokinases which have the property of catalyzing the transfer of phosphate from ATP to suitable monosaccharide acceptors to form the corresponding phosphyrylated intermediates. These modified monosaccharides may now enter the stream of

metabolic activities. There are other enzymes also which are involved in the glycolytic processes.

Metabolism is controlled by the physiological coordination of various active agents in the body. The active agents may be classified as hormones, enzymes, and vitamins. A close physiological interrelationship between the different principles seems to exist. It now appears that the hormones function as regulators of metabolism by modifying the rates of specific enzymatically catalyzed biochemical reactions.

Thyroid has been recognized since long as influencing the metabolic rate in the animal body. Obviously, the effect of the hormone may be by modifying the normal metabolic processes, by effecting the enzyme concentration in the tissues. It has been shown that the thyroid status influences other endocrine organs also and thus modification in the thyroid hormone secretion rate would simultaneously modify the secretion of other endocrine glands as well. Thus the metabolic change attributed to the change in thyroid status may be either directly due to change in concentration of its own secretion or due to modified concentration of the secretions of other glands.

An attempt was made to evaluate the part played by the different glands in the metabolic changes caused by lowering the secretion of thyroid gland i.e. by inducing hypothyroidism. In a series of experiments, hypothyroidism was induced in male rats by incorporating thiourea in the feed of the animals in one group. Animals in another group served as pair fed control. The ration consisted of mixture as shown below ;

Crushed wheat ...	...	6 gms.
Whole milk with 0·5% mormite	...	7·5 c. c.
Sugar ...	...	2·0 gms.

Water was given ad lib.

Induced hypothyroidism caused by feeding thiourea causes a decrease in food consumption. It is well known that food has a significant effect on the various metabolic processes. Defective nutrition has long been known to cause a deleterious influence upon the reproductive system of the male. The defective nutrition causes a change in the hormonal balance in the body and this effects the functioning of the accessory sex organs[2]. A state of "pseudo-hypophysectomy" was described by Mulinos and Panerantz[2] in rats as a result of a diet which was qualitatively adequate but halved in quantity. Further supporting evidence was later provided by several groups where fructose and citric acid in the accessory sex glands was reduced to a castrate level. By treatment with testosterone propionate (0·2 mg daily for one week) or with chorionic gonadotrophin (200 units every other day for two weeks), the secretary activity of the glands could be completely restored.

Considering all these factors the influence of food on the metabolic processes was removed by pair feeding the animals in the thiourea fed and control groups. Thiourea feeding was continued for a period of 28 days. The amount of thiourea fed was also varied in different experiments to find the changes in metabolic processes at different levels of hypothyroidism.

It has also been shown by Reis and Halerston[3] that if rats were exposed to a cold environment for a short period of time, there was an increase in the phosphate

labeled with radioactive phosphorus p^{32} into the total acid soluble fraction of the adrenal gland. Since both the injection of ACTH and exposure of the animals to cold for short periods of time caused an increase in the incorporation of p^{32} into the acid soluble phosphorus of the adrenal, it was suggested that the early phase might indicate an increase in the metabolism of the adrenal brought about by release of endogenous ACTH from the pituitary gland. There is possibility that the increase in the incorporation of p^{34} into the acid soluble phosphorus fractions in adrenal gland might be due to an increased activity of the thyroid. The changes observed in the adrenal were in the same direction as those reported for muscle[4] and liver[5] during hypothyroidism produced by the administration of dried thyroid. There is also good evidence that the thyroid gland is more active after an animal has been exposed to the cold for a period of days.

Adrenal response, to thiouracil treatment caused a reduced P^{32} incorporation, which was reversed by thyroxine, in animals maintained at room temperature [6].

In view of this intimate relationship existing between thyroid and adrenal activity we carried out the following analysis of the adrenal gland in order to evaluate adrenal status in hypothyroid conditions. Adrenal cortex hormones profoundly affect body metabolism by its influence on phosphorylating mechanism.[7]

Following table shows the analysis of the adrenals and seminal vesicles when 15 mg thiourea was incorporated in the feed of the young male rats and the experiment was conducted for a period of 28 days.

TABLE I

Analysis of adrenals and seminal vesicles.

(Results are expressed in mg in the whole gland)

	Adrenal				Seminal Vesicles	
	% Moisture	Ascorbic Acid (mg)	Cholesterol (mg)	Frutose (mg)	Inorganic Phosphorus (mg)	Ascorbic Acid (mg)
Experimental ... Group ...	74·34 ± 1·34	0·01696 ± 0·0007	0·617 ± 0·044	Trace	0·0599 ± 0·0082	0·0263 ± 0·0099
Control ... Group ...	73·19 ± 1·04	0·02781 ± 0·0017	0·773 ± 0·057	0·1809 ± 0·0200	0·0948 ± 0·0072	0·0554 ± 0·0034
Statistical Significance ...	Not Significant	Highly Significant	Highly Significant	Highly Significant	Highly Significant	Highly Significant

[393]

TABLE II

Analysis of adrenals and seminal vesicles

(Results expressed in mg per 100 mg of adrenal and per 100 gm of seminal vesicles)

	ADRENAL			Seminal vesicles	
	Ascorbic Acid	Choles- terol	Fructose	Inorganic Phosphorus	Ascorbic Acid
Experimental Group ...	0·2674 ± 0·227	8·759 ± 0·645	Trace	23·750 ± 1·758	12·78 ± 1·483
Control Group	0·2884 ± 0·0221	7·091 ± 0·671	40·50 ± 2·176	20·740 ± 0·829	12·91 ± 0·623
Stastical ... Significance ...	Significant	Not Significant	Highly Significant	Not Significant	Not Significant

In our experiments analysis of seminal vesicles showed a highly significant decrease in the fructose content of the thiourea fed group. Inorganic phosphorus content was also markedly reduced.

Fructose is the sugar which is found only in the semen and is the nutrient for sperms. Ordinarily, other tissues metabolize sugar in form of glucose and not fructose. The sperm nutrient is synthesized in the accessory sex organs such as seminal vesicles, prostate and coagulating glands. This is obviously obtained from the glucose of the circulating blood.
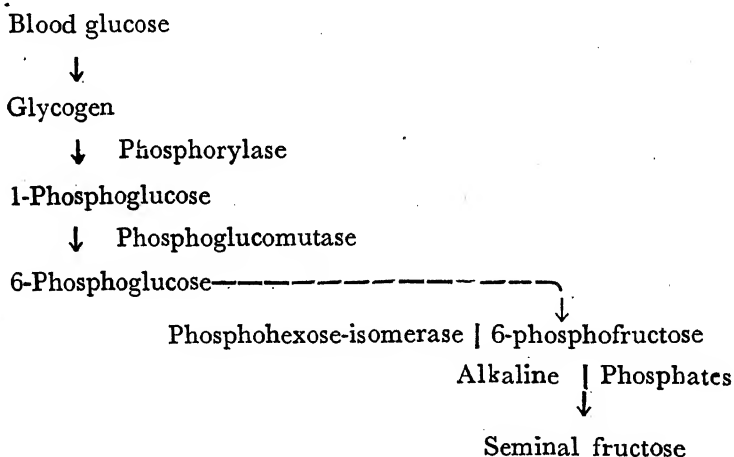
The 'fructose test' originally described by Mann and Parsons (1947) subsequently developed by others, and found on the observation that the capacity of the accessory organs to produce fructose and, thereby, the actual level of fructose in the seminal plasma, reflects the degree of testicular hormone activity in the male or in this way provides an accurate indicator of endocrine testicular function[2]. In our experiments also the histological examination of the testes of hypothyroid rats showed a decreased spermatogenesis. It is concluded that the elaboration of gonadotrophine by the anterior pituitary were also decreased due to hypothyroidism and thus both the testosterone production and spermatogenesis by testis were decreased. In the succeeding experiments we also found a marked diminution in the Inorganic Phosphorus and Ascorbic acid content of the testis as well. Ascorbic acid content of pituitary and seminal vesicles was also found reduced in the hypothyroid male rats.

In addition to the hormone of the testis and the pituitary gland, yet another organ, the pancreas, exerts a profound influence upon the level of fructose in semen[7] The effect is an indirect one, and is brought about by the action of insulin on the level of blood glucose which in turn governs the level of fructose in semen. Insulin induced fall in blood glucose was followed by a reduction in the fructose content of semen. Diabetes induced by alloxan treatment caused an increase in the fructose content of semen.

The experimental evidence available at present brought out the essential, rule of the testicular hormone in the formation of fructose by the secretory apparatus of the male accessory glands, and indicated that blood glucose is the precurssor of seminal fructose. Further details of the mechanism whereby glucose is converted in the accessory gland tissue to fructose, were obtained from in vitro experiments; these showed that small amounts of fructose are formed as a result of incubation of minced accessory gland tissues with glucose, and that these tissues possess the entire enzymic system which can convert glucose to fructose.

It is an established fact that certain phosphorylated derivatives of fructose, such as 6-phosphofructofuranose and 1:6-diphosphofructofuranose, are formed as intermediary substances in the normal carbohydrate metabolism of muscle, liver and other animal organs. However, in the majority of animal tissues these phosphofructoses do not yield free fructose, but are metabolized further to form pyruvic acid and lactic acid. In the semen however, there are present in high concentration enzymes which belong to the group of phosphatases and include the 'alkaline' phosphatase; the latter capable of splitting a number of phosphohexoses, including 6-phosphofructose, 1-phosphofructose and 1:6-diphosphofructose, to phosphoric acid and free fructose. The alkaline phosphatase found in semen is drived from several accessory organs of reproduction but its principal source is the seminal vesicle. Owing to this fact, the usual channels of carbohydrate metabolism are diverted in the vesicular tissue. Phosphofructoses are not metabolized to lactic acid, as would be the case e.g. in muscle, but are dephosphorylated instead so that free fructose is formed.

The enzymic reactions involved in the conversion of blood glucose to seminal fructose are as follows:

Blood glucose

↓

Glycogen

↓ Phosphorylase

1-Phosphoglucose

↓ Phosphoglucomutase

6-Phosphoglucose————————————————⌐
                                      ↓

Phosphohexose-isomerase | 6-phosphofructose

Alkaline | Phosphates
↓

Seminal fructose

In our experiments it was found that the phosphatase activity of seminal vesicles of the thiourea induced hypothyroid rats, as measured by Gomeris histochemical method, was markedly reduced. As already indicated before inorganic phosphorus content of the gland was also reduced in the hypothyroid rat.

The reduction observed in the ascorbic acid content of the gland in the hypothyroid rat might be in some way related to the changes in the metabolic processes in the gland. No satisfactory explanation can be given at present in this regard.

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MINERALISATION OF ORGANIC PHOSPHORUS UNDER TROPICAL CONDITIONS

EFFECT OF PLANT GROWTH ON MINERALISATION

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The importance of organic P in plant nutrition is still a question which needs experimentation. In the past a general opinion was that organic P like calcium apatite and other inorganic unavailable substances is also an unavailable type of synthetical product of microbial origin. The recent trend of the role of organic P in plants nutrition is entirely different. It is now accepted that organic P gets mineralised in soils and liberates inorganic P for plant assimilation[4,10]. The importance of organic P was not realised because most of the experiments were conducted in colder climate of the temperate regions where mineralisation is not so rapid and that is why there is a tendency of accumulation of organic phosphorus in those soils. In hot tropical countries the organic P is an important factor in the availability of P, to plants[2,7] It is also found that a critical value for mineralisation (org. C/org. P=170) also exists[10].

The effect of super Phosphate and other inorganic fertilizers is very short timed in tropical countries like India. The cause of such a thing appears to be the trend of all tropical countries towards alkalinity and formation of apatite forms of reversion Phosphates. Most of the manuring under Indian conditions is by organic P present in F. Y. M. and compost and dispute little resources of P in our soils the manure proves efficient. This gives strong indication to the effect that organic P is principal source of P to plants under Indian conditions. Study of the mineralisation of organic phosphates in presence of growing plants therefore seems quite important for the proper assessment of the role of these phosphates in plant nutrition. In the present investigation the study of mineralisation of organic phosphates in presence of growing plants is made.

METHODS AND MATERIALS

Six soil samples chosen for the purposes were obtained from Banaras and Satna District. Thay were mixed with yeast powder at a rate of ·02%. Sigcol glass beakers were taken up and filled up with 100 gms. sand and above the sand layer soil along with treatments was placed. Healthy wheat, Barley and Pea seeds were obtained from the B. H. U. Farm and twenty seeds of each were sown in different beakers. This was purposely done so that the greater number of plants would eliminate the effect of available inorganic P present in the soil. Hoagland and Snider's solution was added at proper times. Controls containing the different mixtures were left for studying the mineralisation under atmospheric conditions. Analysis of soil was made after 0,15, 20, 25, 30 days. Plants were removed after various periods of growth and were carefully washed and dried. Total P in soil

was determined by Ian armstrong and Black's modified waren Pughs method [6] Total P in plants was determined by ashing with Magnesium Nitrate and developing the colour in the solution by Dickman and Bray's method [1] Hydrolysable P was determined by treating soil with 1 K_2 CO_3 at 80°C for one hour. To an aliquot from this 3C. C bromine water is added and boiled for two minutes. The hydrolysed P is determined colorimetrically [2] Total organic P was determined by the method of Pearson[8].

<div align="center">RESULTS</div>

<div align="center">Decomposition of Total organic P in presence of plants.</div>

Plants help to a great extent the mineralisation of organic P materials. If the temperatures are high the activity may be much more and that is why tropical countries show a considerable mineralisation of organic P in soils [10]. It appears fairly good amount of mineralisation of organic P in soils which are cultivated is due to the secretions of the root systems that they possess. Soil where Pea plants were grown the activity seems to be much. The organic P added as yeast at the rate of ·02% P was almost totally mineralised by 20 plants in about 15 days time. It appears that root systems of pea plants are producing lots of exogenic enzymes to bring about the hydrolysis. In table No. 1 the results of hydrolysis caused by pea plants are very remarkable. The value was 264 p. p. m. in the beginning but it went down to 56, 19, 12, and 8 in 15, 20, 25, 30 days time. In wheat plant cultures the hydrolysis is little and increases with time. The rate of hydrolysis is very much slower and fairly large amount of organic P are left out even after 30 days. The organic P decreased in this case from 264 p. p. m. to 239, 204, 162, 97, p. p. m. in 15, 20, 25, 30 days time. On making deductions for microbial decompositions the decompositions due to plant will come to 25, 60, 119, p. p. m. after 15, 20, 25 and 30 days time. In Barley plants the decomposition is quick but comparatively much less from that of pea. The organic P concentration in this case decreased from 264 p. p. m. to 186, 130, 85, and 38 p. p. m. in 15, 20, 25, 30 days time. If deductions for decomposition by microbes (shown in the control) are made the values 54, 101, 137, 175 represent decomposition by Barley plants alone after 15, 20, 25, 30 days time. The hydrolysis is quite considerable.

The rates of decomposition by plants are shown in table No. 2. In pea plant cultures the rate was maximum in fifteen days i.e. 0·69 p. p. m. per day but after this period it has gone down to ·37, ·07, ·04 in 20, 25, and 30 days time. This rapid decrease in decomposition rate indicates that organic P concentration was limiting. Similarly Barley plants after twenty days show a limiting condition. In soil $\times$ 1, the value was ·26, ·56, after 15 and 20 days time, but at 25th and 30th day the values are ·45, and ·47 respectively. In Wheat plants the organic P concentration is not limiting even after 30 days of time, because the rate was slower and increased slowly. The values in soil $\times$ 1 were ·085, ·33, ·44, ·68 in 15, 20, 25, 30 days time.

It appears from the results that organic P concentration may get limiting to Barley and Pea. The hydrolytic activity seems to be in the following order: —

<div align="center">Pea   >   Barley   >   Wheat</div>

Hydrolysable aad unhydrosable organic P decomposttion

The decomposition of hydrolysable organic P is very quick. In case of pea plants the hydrolysable organic P went down from 160 to 0 in 15 days time (Table

Decomposition of yeast powder in presence of Wheat, Barley and Pea plants.

Sample	Time days	Total P p. p. m.	Hydro P p. p. m.	Unhydro P p. p. m.	Total org. P p. p. m.	Inorg. P p. p. m.
100 gms. soil (XI) ...	0	676	160·0	104·0	264·0	412
·02% P. Control ...	15	676	122·0	119·0	240·0	436
	20	676	109·0	122·0	231·0	445
	25	676	101·0	120·0	222·0	454
	30	677	93·0	120·0	213·0	464
Pea plants grown ...	0	676	160·0	104·0	264·0	412
	15	666	0·0	56·0	56·0	610
	20	613	0·0	19·0	19·0	594
	25	556	0·0	12·0	12·0	544
	30	527	0·0	8·0	8·0	519
Barley plants grown ...	0	676	160·0	104·0	264·0	412
	15	666	70·0	116·0	186 0	480
	20	662	46·0	84·0	130·0	532
	25	656	21·0	64·0	85·0	571
	80	630	0·0	38·0	38·0	592
Wheat plants grown ...	0	676	160·0	104·0	264·0	412
	15	674	120·0	119·0	239·0	435
	20	672	86·0	120·0	206·0	466
	25	659	63·0	99·0	162·0	497
	30	631	14·0	80·0	94·0	537

Average decomposition of organic P by single plant in p. p. m. per day

Sample	Time days.	soil ×1	soil ×2	soil ×3	soil ×4	soil ×5	soil ×6
Soil alone ...	15	·08	·11	·08	·145	·073	·10
	20	·09	·12	·11	· 17	· 14	·11
	25	·09	·12	·10	· 16	· 13	·09
	30	·09	·11	·09	· 16	· 13	·08
Pea plants ...	15	·69	·675	·655	·605	· 69	·675
	20	·37	· 13	· 12	·070	· 29	· 24
	25	·071	· 07	0·06	·075	· 06	· 11
	30	·040	·05	·06	·040	·05	·04
Barley plants ...	15	· 26	·385	·27	· 29	·26	·26
	20	· 56	· 48	·34	· 45	·45	·46
	25	·45	· 48	·40	· 46	·49	·48
	30	· 47	· 27	·40	·070	·49	·49
Wheat plants ...	15	·085	· 12	·085	·15	·075	·105
	20	· 33	· 28	· 36	· 43	·38	· 26
	25	· 44	· 47	· 42	· 45	·40	·50
	30	· 68	· 55	· 63	· 46	·61	· 61

No. 1). With barley plants a zero was attained after 30 days and with wheat plants it may take a longer time. The value in this case went down from 160 to 14 in 30 days time. It is observed that hydrolysable organic P is decomposed first in the initial stages, but with time some unhydrolysable organic P is also decomposed. In all the cases of decompositions studied here the unhydrolysable organic P shows an increase in the initial stages at the expense of hydrolysable phosphorus. The value went up from 100 to 119 in soil and wheat culture, but in barley to 116 p. p. m. In the pea cultures due to heavy activity it went down.

Uptake of P and amount of organic P hydrolysed by plants.

The uptake and organic P decomposed in miligrams by 20 plants is shown in table No. 3. In pea plants cultures the uptake by plants is less than the amount

of organic P decomposed in 30 days time. In soil XI 15·1 mgm. is the uptake against the decomposition of 25·6 mgms. of organic P. In barley cultures the uptake of P is less than that of pea plants, but the organic P decomposed is of a lesser degree in the early stages. In soil XI 4·5 Omgms is the uptake against 2·26 mgms. decomposition of organic P. In wheat cultures the decomposition is much less and uptake very little in the beginning (·22 mgms. in 15 days). After 30 days P is assimilated in fairly good quantities and attains a value equal to Barley.

In all instances discussed above organic P hydrolysis it appears is independents of the amount of P taken and in no case can be attributed to the requirements of plants for P. It will be seen that pea plants effect hydrolysis of almost entire quantity of organic P added and closely followed by barley plants, while the wheat plants are much slower about hydrolysis. The uptake by the three groups of plants are not however, in the same order even the most effective group i.e. pea plants utilized only about 60% of the amount hydrolysed during first 30 days, while barley and wheat take up even much less proportion.

TABLE No. 3

Uptake and decomposition of organic P compounds in mgms. by 20 plants grown in different soils after 30 days of growth.

Sample No.	Pea plants		Barley plants		Wheat plants	
	Uptake of P mgms.	Decomp of org. P mgms.	Uptake of P mgms	Decomp of org. P mgms.	Uptake of P mgms	Decomp of org. P mgms.
X1	15·1	25·6	14·6	22·6	4·57	17·7
X2	15·08	22·7	4·7	20·8	11·2	16 7
X3	9·97	22·2	3·63	19·5	3·1	14·6
X4	12·45	20·0	4·66	18·5	4·25	16·8
X5	18·0	24·7	4·96	22·2	4·33	16·2
X6	8·8	24·3	3·3	21·1	3·06	15·8

DISCUSSION

The plants play as important role in P mobilisation by their hydrolytic activity. The available organic P is thus utilized by them. The plants have an inherent proparty to produce exogenic enzymes and the amount and type of enzymes produced by them will determine the hydrolytic activity caused by them (9). The various types of organic P compounds which can be found in natural products are:—

(1) Phospholipins (2) Phosphoproteins (3) Nucleic acid, (4) Phytin (5) Sugar phosphates and it appears plants can utilise them. The process may be well marked under tropical conditions where more of enzymatic activity is expected due to the high temperatures.

Yeast powder contains Nucleic acid P as principal source of P and wheat, Barley, and pea plants grown on this provide a differential behaviour with regard

to its hydrolysis. The pea plants cause a quick and maximum activity and next in order comes Barley. With wheat, however, it was least. It, therefore, seems not impossible that for pea plants Nucleic acid is as good a form of P as any other easily available P. In early stages of decomposition only hydrolysible organic P is decomposed. It is observed that immediately after addition of organic P to soil certain hydrolysable org. P gets fixed up as unhydrolysable. Recently Goring and Barth olomew have shown that Nucleic acid P gets adsorbed on clays through orthophosphate and Cationic groups (5). It appears such a fixation occurs in soils but the adsorbed P can be released by plants as is indicated by results. The hydrolysable organic P in the present case is partly of the form of a sugar phosphate and hydrolyssis takes place continuously even in control series. The actual agent may be enzymic or microbial. The remarkable difference in this activity created by different plant species requires explanation. The wheat plants show practically no appreciable increase in the rate of decomposition of this fraction in the first 15 days period being only as much as in the control. Greater action is, however, obtained in the later periods and it appears as though the organic hydrolysable P in the absence of available inorganic forms stimulates to specific enzyme secretion. The utilization of hydrolysable form brings about more distinctly this difference. The wheat and Barley plants are able to make use of this form of organic P to a lesser extent, while pea plants show a distinct capacity to utilise even unhydrolysable form. It appears possible, therefore, to distinguish plant to plant on the basis of utilization of hydrolysable forms of organic P. A consequence that would follow may be that specific composition of organic P material will be necessary to meet the requirements of particular plant.

The result of uptake indicate a lag in the absorption of the hydrolysed P. It seems that the hydrolysis is considerably in excess of plant requirements and the released P gets fixed up as in the case of any water soluble in organic P applied to soils and becomes very slowly available to plants.

It is interesting to note that organic P compounds once considered unavailable products are so important in plant nutrition. Like Nucleic acid, phospholipins and phytins are also important for plants. The results of these findings shall appear in my next communication.

SUMMARY

Decompcsition of organic P in soils was studied in presence of growing plants. The plants are able to hydrolyse much more of organic P than the micro-organisms. A differential behaviour regarding hydrolytic Activities was marked and the order is pea > Barley > wheat. The utilization of P appears to be independent of hydrolyssis, caused by the enzymes of root systems. It is indicated that under tropical conditions organic P may be important in plant nutrition.

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ADSORPTION OF MONOCALCIUM PHOSPHATE BY SOILS, BENTONITES, LIGNITE, HYDRATED OXIDES AND OXIDES OF IRON, ALUMINIUM AND CHROMIUM

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Many mechanisms have been proposed to explain phosphate adsorption by soils and they have been summarized by Wild[1]. They include fixation by iron and aluminium in acid soils either in the form of iron or aluminium phosphate or the adsorption of phosphate ions by the hydrous oxides of iron and aluminium ; the precipitation by divalent cations in neutral and alkaline soils ; the fixation by clay minerals and bond linkage to the clay lattice through the exchangeable cation. Coleman[2] investigated phosphate fixation by montmorillonite and kaolinite and concluded that iron and aluminium were principal fixing agents. Chatterji and Dutta[3] found that the removal of oxides of iron and aluminium greatly decreased the fixation by montmorillonite. Scarseth[4] concluded that bentonites adsorb phosphate by an exchange of phosphate ions for hydroxyl ions at the crystal lattice edge. He was supported by Stout[4(a)] and Murphy[5]. Ravikovitch[6] for the first time proposed the phosphate fixation to be a H_2PO_4-Ca-clay linkage which was supported by Scarseth[7] and Allison[8]. Ellis and Troug[9] opposed this bond theory due to a different behaviour of the magnesium treated soils which should behave like the calcium soils. Wey[10] proposed a link between the peripheral aluminium in the octohedral layer of montmorillonite and $H_2PO'_4$ ions from the soil or phosphoric acid. Damaty and Axley[11] observed a marked adsorption of phosphate from mono-calcium posphate in the presence of KCl and proposed a H_2PO_4-Ca-Soil linkage.

No data are available in which the adsorption of both the cations and anions have been determined. Lignite has not been used as a medium of phosphate fixer so far. The adsorption by chromium oxide has also not been studied. Chromium is abundant in lithosphere (299 p. p. m.) and the chromium content[12] of normal soils varies from 5 to 1000 p. p. m., Hence the adsorption of phosphates by chromium oxide has been studied by us. In this paper, we have recorded our observations on the comparative adsorption of both calcium and phosphate ions from monocalcium phosphate solutions and the effect of phosphate adsorption on the exchangeable cations.

EXPRIMENTAL PROCEDURE

The soils used in these experiments have been designated as good, garden and normal soils depending upon their chemical constituents and fertility. The bentonites were obtained from Kashmir (India) and have been named yellow, green or pink according to their colours. The oxides of iron, aluminium and chromium used, are from B. D. H. company. The hydrated oxides of iron and aluminium were prepared by precipitation from the chlorides of iron and aluminium by ammonium hydroxide washing them free of excess of ammonia and making a suspension in water. 20 c.c. of the suspensions of hydrated oxides of iron and

aluminium containing 0·5798 gms. Fe$_2$O$_3$ and 0·485 gm. Al$_2$O$_3$ respectively, were used in adsorption experiments. 12·5 gms. of the soils, 5 gms. of the bentonites, 5 gms. of the oxides and 12·5 gms. of lignite were taken and 100 c.c. of monophosphate solution was added. The contents were shaken for two hours and filtered after 24 hours. The filtrate was analysed for calcium and phosphate contents. These amounts were subtracted from the original calcium and phosphate contents in 100 c.c. monocalcium phosphate solution. The differences gave the adsorption of the cations and anions and from these values the adsorption per 100 gms. of the materials was calculated. The percentage of the adsorbed cations and anions from the orginal solutions has also been given. The chemical analyses of the materials and the exchangeable bases are recorded in table 1. The treated soils, lignite and bentonites were washed free of the soluble phosphate solution with alcohol, oven dried and analysed for the exchangeable bases using Normal ammonium acetate. The standard methods of the analyses of bentonites, soils and lignite have been followed[12-19].

RESULTS

TABLE 1.

Chemical composition, pH and the exchangeable bases of the materials used for adsorption experiments.

Materials	Total Carbon %	Sesqui oxides %	Fe$_2$O$_3$ %	CaO %	MgO %	P$_2$O$_5$ %	pH	Exchangeable bases m.e./100		
								Ca	Mg	K
Normal soil	0·44	11·17	4·12	0·992	1·16	0·079	7·6	22·76	3·02	2·43
Garden soil	0·20	9·86	4·26	2·800	1·73	0·122	8·0	44·64	3·62	2·00
Good soil	1·44	9·83	4·35	4·080	1·77	0·418	7·6	48·71	6·94	3·14
Lignite	...	3·60	...	0·987	0·18	0·051	4·8	31·03	9·00	1·40
Yellow bentonite	32·83	10·66	1·900	2·48	1·004	7·9	8·48	27·15	2·10
Green bentonite...	31·10	11·65	2·600	5·43	0·176	9·1	38·78	18·39	3·41
Pink bentonite ...	22·92	1·97	2·540	2·62	0·041	7·7	76·40	30·73	1·90

TABLE 2(a)

Adsorption of monocalcium phosphate

Materials	M/100 $CaH_4(PO_4)_2$		M/200 $CaH_4(PO_4)$		Adsorption of H$_2$PO$_4'$ ions. M/500 $CaH_4(PO_4)$	
	Adsorption per 100 gms. of the materials.	% adsorbed	Adsorption per 100 gms. of the materials.	% adsorbed	Adsorption per 100 gms. of the materials.	% adsorbed
Soils						
Normal ...	0·3240	31·6	0·1474	27·3	0·0632	29·3
Garden ...	0·4096	40·0	0·1593	28·1	0·0421	19·5
Good ...	0·3552	34·6	0·1392	25·8	0·0332	15·4
Bentonites						
Green ...	0·5644	20·0	0·3248	22·9	0·1139	20·1
Yellow ...	0·5839	20·7	0·2977	21·1	0·1677	29·8
Pink ...	1·1950	42·3	0·6683	47·4	0·2195	38·8
Lignite ...	0·0917	9·0	0·0939	16·6	0·0607	28·1
Oxides						
Iron ...	0·3327	11·8	0·2155	15·3	0·1750	31·0
Aluminium ...	0·5106	18·1	0·3720	26·4	0·2011	35·3
Chromium ...	0·5586	19·8	0·4503	31·9	0·2795	49·5
Hydrated oxides						
Iron ...	19·3700	82·5	10·9800	92·9	...	100·0
Aluminium ...	15·5100	55·0	10·6600	75·6	...	100·0

TABLE 2(b)

Adsorption of Ca ions.

Soils						
Normal ...	0·1250	40·9	0·0256	16·6	(−)0·0009	(−) 1·5
Garden ...	0·1454	47·6	0·0386	25·0	(−)0·0057	(−) 9·3
Good ...	0·1470	48·1	0·2190	14·4	(−)0·0062	(−)10·5
Bentonites						
Green ...	0·7162	93·7	0·3780	98·0	0·1545	100·0
Yellow ...	0·6960	91·6	0·3800	100·0	0·1600	100·0
Pink ...	0·4142	55·0	0·2042	53·7	0·0520	30·2
Lignite ...	0·0889	29·0	0·0545	35·3	0·0100	26·0
Oxides						
Iron ...	0·0198	2·6	...	...	...	...
Aluminium ...	0·1950	25·6	0·1136	29·8	0·0680	42·5
Chromium ...	0·0900	11·84	0·0504	13·26	0·0.40	3·0
Hydrated oxides						
Iron ...	4·8300	70·0	2·6600	77·4	...	...
Aluminium ...	4·1200	50·0	2·5200	61·6	...	...

TABLE 3.

Exchangeable bases of the phosphate-treated materials.

	M/100CaH$_4$(PO$_4$)$_2$			M/200 CaH$_4$(PO$_4$)			M/500 CaH$_4$(PO$_4$)$_2$		
	Ca^{++} m.e.	Mg^{++} m.e.	K$^+$ m.e.	Ca^{++} m.e.	Mg^{++} m.e.	K$^+$ m.e.	Ca^{++} m.e.	Mg^{++} m.e.	K$^+$ m.e.
Soils									
Normal	18·3	2·9	2·2	20·6	3·0	2·3	20·3	3·5	2·4
Garden	30·2	2·0	1·9	24·9	2·1	2·0	29·3	3·0	2·0
Good	38·2	3·0	2·8	31·3	5·0	3·0	31·0	5·8	3·1
Lignite	36·0	3·0	1·4	34·4	5·2	1·4	31·5	8·0	1·4
Bentonites.									
Green	91·5	19·0	3·1	82·0	21·7	3·2	53·3	19·3	3·3
Yellow	62·7	20·6	2·0	45·7	27·1	2·1	15·6	26·4	2·1
Pink	103·9	19·9	1·8	88·6	25·6	1·8	82·1	26·2	1·9

DISCUSSION

From a survey of the table 2(a) & (b), it is clear that the highest adsorption of phosphate ions takes place in hydrated oxides of iron and aluminium. The bentonites and the oxides of iron, aluminium and chromium show almost similar adsorption. Of the bentonites, the pink variety adsorbs the highest quantity of phosphate and of the oxides, the chromium oxide shows the greatest adsorption. Of the soils, the garden soil appears to adsorb the highest amount of phosphate.

However, the adsorption of calcium ions takes place in a different manner. The soils at the lowest concentration do not adsorb any calcium ion but show a negative value. The bentonites adsorb calcium ions even at the lowest concentration of calcium ions and there is cent per cent adsorption of calcium ions from the lowest concentrations. The oxides of iron, aluminium and chromium also adsorb calcium ions but the adsorption is not very marked. The hydrated oxides of iron and aluminium appear to be very active adsorbents of calcium ions. Lignite shows a fair adsorption of calcium ions.

The exchangeable calcium in the phosphate-treated soils decreases to a great extent at all dilutions. Lignite shows an increase in the exchangeable calcium. The bentonites appear to have quite different values. The exchangeable calcium increases while the exchangeable magnesium decreases but the increase in exchangeable calcium is not proportional to the decrease in exchangeable magnesium. It appears, therefore, that the calcium adsorbed from the monocalcium phosphate solution displaces some of the magnesium from the exchange-complex of the bentonites but the majority of calcium is adsorbed at the edges of crystal lattice in exchangeable form. In this respect the bentonites differ from the soils, which adsorb calcium and at the same time their original exchangeable calcium decreases. Hence it can be concluded that the adsorbed phosphate combines with exchangeable calcium to form insoluble dicalcium and tricalcium phosphates. The adsorbed

calcium ions also appear to take part in the formation of these insoluble phosphates of calcium because the adsorbed calcium is not in the exchangeable form. The presence of oxides of iron and aluminium and chromium in the soil is also responsible for the phosphate adsorption because the table 2(a) shows that they adsorb phosphates in amounts almost equal to the soils. The presence of free hydrated oxides cannot be expected in soils because the hydrated oxides show a very marked phosphate adsorption.

The bentonites show a preferential adsorption both for phosphate and calcium ions. They possess the properties of both sesquioxides and soils. The chemical composition of bentonites shows that they are rich in sesquioxides. High exchangeable calcium in the case of pink bentonite accounts for a high phosphate adsorption as well as a smaller calcium adsorption. The lignite is peculiar in its behaviour because it is acidic and has equal adsorptive powers both for calcium and phosphate ions.

From our adsorption experiments it is also clear that though the adsorption of phosphate increases as the concentration of phosphate solution is increased, the soils and bentonites do not adsorb more than 30-50% of the phosphate ions present in the monocalcium phosphate solutions. Even the oxides of iron, aluminium and chromium do not adsorb more than 50% of the added phosphates. The hydrated oxides being freshly precipitated and very reactive are able to remove all the phosphate from more dilute solutions.

A marked preferential adsorption of phosphates at lower concentrations by the soils is evident from the fact that they show a positive phosphate adsorption while a negative calcium adsorption.

Thus it is clear that the soils, bentonites and oxides of iron and aluminium show a similar adsorption of phosphate ions because the soils contain both the oxides and the clay minerals like bentonites and kaolinite. But the dissimilarity in calcium adsorption shows that our soils are not rich in bentonites or montmorillonite. There is always a decrease in the exchangeable calcium by the phosphate treatment of the normal soils.

SUMMARY

Adsoption of calcium and phosphate ions from dilute solutions of mono-calcium phosphate has been studied using soils, bentonites, lignite, oxides of iron, aluminium and chromium and hydrated oxides of iron and aluminium. It has been found that hydrated oxides adsorb the highest amount of phosphate ions whilst bentonites, soils, lignite and oxides of iron, aluminium and chromium show almost similar adsorption.

The preferential adsorption of phosphate by soils and equal adsorption of calcium and phosphate by bentonites has been observed.

The treated soils show a marked decrease in their exchangeable calcium content whilst the bentonites and lignite show a marked increase in it. It appears, therefore, that the phosphate ions adsorbed combine with the exchangeable calcium and the adsorbed calcium to form insoluble phosphates and thus decrease the exchangeable calcium in soils.

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EFFECT OF PHOSPHATE FERTILIZERS ON WHEAT

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My friend and colleague Dr. Das has already spoken about the role of phosphate *vis a vis* the plant. He undertook this study on barley while I propose to deal with the effect of phosphate fertilizer on wheat, and this too on the basis of the amount of total phosphorus present in the soil at different stages during its life cycle. An attempt, in the present investigations has been made to correlate soil phosphate with vegetative growth and grain yield. Phosphate at five different levels ranging from 20-100 lbs. P_2O_5 per acre was applied along with a no-treatment which served as a control.

The total phosphate in the soil at the first stage was found to increase upto P_{80} treatment, after which there was a decrease. A similar trend was recorded at the second stage with the exception that maximum increase was observed only in P_{60} treatment. It was followed by a decrease in higher treatments. An identical trend was seen at the third stage.

It is seen that higher application of phosphate results in higher uptake. Similar findings have also been reported by Teakle (1929) and Carolus (1933). That higher application results in higher uptake of fertilizer is also supported by the morphological data i.e., decrease in the total soil phosphorus has been associated with increase in plant height, tillers and leaves. Gregory (1937) has also reported increased tillers in barley by phosphate aplication and Reitz and Myers (1944) report increased height for wheat plant.

It is the soil from which the minerals are taken up by the plant and hence amounts of minerals in the soil is of considerable importance. With increasing phosphate concentration there has been increased up take and that soil phosphorus varies directly with that in plants. Mather (1931), Jacob (1935) and others have also reported similar findings.

The effect of phosphate fertilizer has resulted in an increased yield of grain upto P_{60}, after which its higher application has resulted in decrease. The application of phosphate fertilizer increases total yield of grain and it is also suported by soil analysis and morphological data.

It is found that P in the higher treatments showes a lower value indicating that it is being taken up by the plant. But from morphological and yield data it is clear that higher uptake is not benificial to the plant. It seems that above a certain limit plants cease to respond to increased application of nutrients but continue to absorb increasing amount from the soil resulting in luxury consumption. Russel (1923) working with barley found that higher doses of fertilizer decreased yield. According to him decrease in yield is due to hastening in maturation.

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The addition of phosphatic fertilizer results in vigrous growth and higher yield of crops. Similar observations have also been reported by Murphy (1945) and Bartholomew (1948).

Much of the minerals are taken up by the plant in the earlier stages of growth. The maximum uptake of phosphate is at the second stage after which it decreases. Knowles and Watkin (1931) state that it is in the earlier stages that most of the minerals are taken up. Eckerson (1929) stated that probabely in all forms of life, phosphorus seems to stand on the threshhold between potential and kinetic energy. Recent researches have more or less confirmed the observation of Eckerson as P has been found to play important role in photosynthesis, respiration, nitrogen metabolism, etc. Benson and others (1950) have identified phosphoglyceric acid as the first stable product of photosynthesis.

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ROLE OF PHOSPHORUS IN THE SOIL, PLANT AND ANIMAL KINGDOM

By

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To modern man, phosphorus is the all-important essential constituent of all living organisms in general and of vegetable tissues in particular. Phosphorus in agriculture is the story of the indispensable ingredient,—without it agriculture is inconceivable. That is why phosphorus is often regarded as the master key to agriculture. It is present in every living cell and thus essential in both plant and animal nutrition.

Importance of phosphorus in soil and plant

In plants it is mostly concentrated in the seed. It is no less important in soils. An adequate amount of available phosphate in the soil favours rapid plant growth and root development, hastens fruiting and maturity and improves the quality of crops. A deficiency of phosphate in the soil, on the otherhand, restricts root system and developes bronzing or purpling of leaves. Plants deficient in phosphorus cannot absorb enough potassium, and in consequence, cannot have sufficient strength in their straw, leading ultimately to lodging.

Phosphorus is essential for improving the quality of crops and palatability of vegetables. It has a balancing influence on potassium and nitrogen and counteracts the harmful effects of excess of nitrogen by hastening fruiting and maturity and increasing resistance to disease.

Influence of Phosphorus on crop yields

On the strength of about 20,000 experiments between 1926 and 1936, S. Gericke (1939, 1940, 1948) came to the conclusion that 1 kg. of phosphoric acid assimilated by the plant produced in grain 31·5 kg. of plant mass. For potassium, the corresponding yield is 4·1 kg., and for nitrogen, 22·5 kg. In the case of other important agricultural plants such as, potatoes, sugarbeet, etc., it has been confirmed that phosphoric acid gives the highest yield of all plant foods. This is tantamount to saying that the yield drops most, when insufficient phosphoric acid is present in the soil.

Value of phosphorus in plant nutrition

Besides the beneficial effect of adequate phosphorus in the soil on high crop yields as stated above, its value on the nutritional value of food grains is also important. Recently the Tennessee Valley Authority in their soil rehabilitation programmes showed that heavy applications of phosphate to legume fodder crops grown on impoverished soils, increased the growth of legumes and rapidly built up

fertility for the succeeding cereals which previously could not be grown successfully. This increased fertility was due to increased fixation of nitrogen and increased organic matter. For every pound of phosphate, the legumes through the action of symbiotic bacteria were able to fix 3 lbs. of nitrogen. The experiments of Parr and his colleagues (1945, 1947, 1948) of Indian Agricultural Research Institute at New Delhi and Karnal confirmed the above observation by showing that phosphate manuring of fodder legumes not only increased the yields of legumes to which it was applied, but also that of the following unmanured cereal crops. The analysis of the phosphate-treated legumes and of the unmanured cereal crops which followed in the rotation showed higher percentages not only of phosphorus, but also of nitrogen. Tne feeding value of crops thus raised with phosphate manuring was shown to be much higher than that of crops not so manured. Das (1946) also showed that the phosphate content of cereals increased appreciably with the increased applications of phosphatic fertilizer to the calcareous soils of Bihar, while the nitrogen content tended to decrease slightly. The potash content, however, remained unaffected. The increased crop yields were also obtained with the increasing doses of the phosphatic fertilizer.

Phosphorus : Nitrogen Relationships in soil

In this way, phosphorus is raised to the forefront of the soil's requirements, and nitrogen relegated to the second place. If, therefore, judicious care is taken for the proper supply of phosphates to the soil, the nitrogen will look after itself. The whole living kingdom of plants and animals is largely dominated by the phosphate content of the soil. The health and advancement of a nation may be dependent on the amount of phosphorus that can be put into active circulation through the soil.

How poor quality of food grains is related to human health and disease

Again, how the poor quality or nutritional value of food grains carries with it grave risks of malnutrition and endemic disease will be apparent from the following instance stated by Davis (1917). It is well-known that the outbreak of beri-beri is generally regarded as associated with the use as main diet of polished rice containing a deficiency of essential nutritive substances. Whatever may be the nature of the essential constituent which is lacking in polished rice, the percentage of P_2O_5 is generally accepted as an index of the beri-beri producing power of a sample of rice. Rice having 0·47% of P_2O_5 has been found to be a healthy food for fowls, while rice with only 0·28 of P_2O_5 brought about polyneuritis in a few weeks. A sample of rice from Sabour in Bihar contained only 0·27% P_2O_5. There is no doubt that the rices of Bihar and possibly other crops are deficient in this vitally essential constituent of P_2O_5. Both quality and quantity of grain can be improved by the application of phosphate to the soil which is in a dangerously exhausted condition as regards available phosphate.

How soil fertility and crop yields depend on phosphate, affecting men and animals

The deterioration in fertility of Indian soils, particularly with regard to available phosphate, can also be judged from the following instances. In 1907, exhaustive soil analyses of the eastern Gangetic plain of Bihar were carried out at Pusa, the old site of the Indian Agricultural Research Institue, with startling results. These expreiments showed that 40 % of Muzafferpur, 60 % of Saran, 75 % of Darbhanga, and 80 % of Champaran soils contained less than 0·0007% of available phosphate. By this date, the situation might be still worse. Further south in Chota Nagpur

where inhabitants do everything opposed to accepted principles of agriculture, the results are evident ; the cattle have deteriorated to such an extent that they are only useful for drought purposes, the cows produce barely sufficient milk for their calves and their growth is very stunted. As we proceed westwards, both beasts and men improve with an increasing phosphate content of the soil, until in the Punjab it is found that goats give as much milk as four Chota Nagpur cows and are considerably taller, while the difference in physique of the inhabitants must be obvious to anyone. Malformations among the human population of certain districts in Bihar are traced to the defficiency of available phosphate in the soils of these districts and consequent low phosphate content of cereals produced on them. Davis (1917) found that where comparative analyses were available of the same soils of Bihar at intervals during the past 20 years, the rapid falling off of the phosphate content was clearly visible. Wherever manurial experiments were conducted in Bihar (Pusa, Dalsing-Sarai, Dooriah), it was found that superphosphate gave maximum returns, the crops being frequently more than doubled. This impoverishment of the soil with respect to phosphate had its effect not merely on the yield of crops, but also on their quality, and a further fall in nutritive value of crops carried with it grave risks of malnutrition and endemic disease which was already stressed earlier (Cf. Davis, 1917).

Submontane soils in the Punjab are also deficient in available phosphate. Lander and Dharmani (1938) have attributed the poor conditions of animals and various malformations and diseases among the human population of Kangra district to this phosphate deficiency of soils.

Phosphorus as one of the most Important Mineral Nutrients for men and Animals

Thus, phosphorus is not merely a plant nutrient, but also one of the most important mineral nutrients of men and animals. If we could ensure that 50 of the phosphate applied to the soils passed into crops and thence into our foods, we should make an enormous stride, not merely in crop production, but in human and animal health as well, seeing that phosphorus malnutrition is much more prevalent than is commonly supposed.

Phosphorus in its Various soil-plant and soil-animal Relationships

As civilisation becomes more complex, so do food requirements and standards, and as population increases, the demands on the soil increase also. In the future, it will be necessary to guard the soil and its products from deterioration more carefully than ever. To produce the right quantity of food stuffs of the right quality will increasingly tax the energies and resources of scientists and farmers alike in the years to come.

Thus, the role of phosphorus in the nutrition and the world problem of food production is very great. Phosphorus is so basic to the whole problem of crop production that probably no other subject in the field of soil fertility has received so much attention in recent years than the phosphate problem in its various soil-plant and soil-animal relationships. It will probably continue to challenge the best efforts of agricultural scientists for many years to come. The problem, however, has not still received as much attention in India as it deserves.

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PHOSPHATE AND CROP PRODUCTION

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INTRODUCTION

Plant production depends upon the fertility of the soil, which in turn depends upon the presence of nutrients in it and their availability. It is likely that these necessary nutrients may be present in sufficient quantities but it is not their presence but their availability to the plant that is important. This is particularly true in the case of phosphate nutrient. In majority of the soils, it has been observed, that the total phosphate present is quite adequate, but if the quantity of available phosphate is taken into consideration, the soils will have to be classified as "Poor in Phosphate." The main reason for this "Poor" status of phosphate in the soil is that the phosphate already present is in "fixed" condition and due to the fixing character of the soil any amount of phosphate added get immediately fixed making it unavailable to the plant.

It has been observed that "low crop production is due more often to the lack of phosphorus than to the lack of any other element." Phosphate is essential for the healthy growth of plants and animals. Adequate supply of phosphate to the plant helps to ensure rapid growth and early maturity. Animals fed on poorly phosphated crop develop diseases and suffer badly and to overcome this malnutrition phosphate has to be supplied in one form or other directly to the animals. This clearly indicates the importance of phosphate in Agriculture.

PHOSPHATE IN SOILS

Soils vary a great deal in their phosphate status. The deficiency of phosphate is observed in areas where the land is cropped over a long period specially so where grain crops are grown. Acid clay soils low in organic matter lack adequate amount of available phosphate and therefore give greater response when phosphate fertiliser is added to it. Acid soils and soils containing free hydrated oxides of aluminium and iron fix up the added phosphate and thus make it unavailable to the plant. In India the laterite soils of Malabar and lateritic soils of the Nilgiris in Madras State are some of the examples of highly phosphate fixing soils. In America[1] sandy soils of the Atlantic and Gulf Coastal Plains contain less than 500 pounds of phosphorus per acre in the first 6 2/3 inches of soil. Most of fertile soils there do not contain more than 1200 to 1500 pounds per acre. The percentage of phosphorus in the surface soil is found to be about one half of the nitrogen content and 1/20th of Potassium content. In Bombay State, most of the soils on the dry areas of the Deccan are very poor in phosphate the figure for phosphoric acid varying between 0·03 to 0·11% depending upon the soil type.[2] Birrell[3] while studing the problem of phosphate fixation in some New Zealand soils has found that a number of laterites and brown loams have high power for fixing the phosphate permanently and their fixing power is identical.

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The low phosphate status may be sometimes due to the low organic content in the soils but is primarily the outcome of the loss of phosphate through intake by crops and soils erosion. In cereal farming the amount of phosphates removed by grain is about 75% of the phosphate derived by the plant from soil. In the livestock system about 30% of the phosphates in the feed is absorbed and 20% is lost in the manuer. *This indicates that only about half of the phosphorus given to the plant is returned* to soil when the livestock is grazed in Situ. Kanitkar and associates[4] have found that 1000 pounds of dry matter of Jowar (sorghum) removes about 2·8 pounds of phosphoric acid. In the manurial trials conducted in Madras State India[5] it has been observed that Paddy and Potato remove about 22 pounds of phosphoric acid per acre.

As already mentioned in addition to the phosphate removed by crop and live-stock farming, severe losses accrue from soil erosion also. It has been observed that continuous cereal cropping makes the land more susceptible to erosion and data collected at the Dry Farming Research Station, Sholapur (Bombay State) have shown that the 7 inches of surface soil is removed within 27 to 42 years under continuous cereal cropping. This loss of soil and the runoff from such cultivated fields carry along with them a large amount of nutrients. Basu [6] has compared the losses of different fertility constituents occuring from the plots under natural vegetation and cultivation of Jowar. The following table illustrates the point.

Loss of different fertility constituents in pounds per acre.

Constituents	Natural Vegetation		Cultivation of Jowar	
	Runoff	Silt	Runoff	Silt
Nitrogen (N)	0.25	1·41	0·16	126·95
Phosphoric acid (P_2O_5)	0.62	0·79	0·78	129·89
Potash (K_2O)		7·79		1273·3
Lime (CaO)	31·83		44·42	8521·1

In U. S. A. also it has been noticed by Miller and Krusekopff[7] that where corn was grown continuously on land having 3·7 per cent slope, phosphorus lost in one year through erosion is much more than is found in 75 bushels of corn. They have further observed that even when a good rotation is followed the loss through erosion is equivalent to the amount found in 25 bushel of corn. Lipman and Conybeare[8] have estimated that U. S. A. loses about 2 million tonis of phosphorus through erosion. These figures show the gravity of the situation and the necessity of conserving the soil and careful saving of the phosphates in the soil and addition of phosphates in the form of manure or fertilizers.

PHOSPHATE FERTILIZATION AND CROP PRODUCTION

As mentioned earlier, soils of Dry Farming areas in general lack in phosphate supply either on account of excessive and continuous cropping of cerealsl or as a result of severe soil erosion. Basu and Puranik[9] have estimated that nearly 40%

of the Dry Farming areas of Bombay State has undergone severe or moderate erosion and has therefore lost most of its fertility. Basu, Rege and Deshpande [19] have found good responses to the application of Phosphate in these arid soils as a result of experiments conducted at Agricultural Research Station, Sholapur, and its substations. The does of phosphate adopted in these experiments was 25 pounds of P_2O_5 per acre. This has resulted in an increase of about 35% in yield in Sholapur soils and nearly 45% in the soils of chas which are very poor in phosphates. They have also noticed that the effect of phosphate is greatly pronounced when it is combined with organic manures like groundnut cake and Farm Yard Manure. The increase in yield was found further enhanced in general by about 20% in such cases. This beneficial effect is probably due to the production of certain organic acid anions which form compounds with free iron and aluminium and the resultant reduction in fixation of phosphates supplied or the release of already fixed phosphates on replacements.

A fairly good percentage of arid soils contain lime but little of organic matter. Such high contents of lime convert the applied phosphates into complex forms of low solubility which however are capable of transition into available phosphates under favourable soil conditions. This change or fixation is chiefly brought out by the calcium present excessively in soils and conversion of phosphates into compounds of carbonates, hydroxi fluoride and sulphates. When a more easily soluble phosphate like super phosphate is applied to a calcareous soil or excessively prelimed land, the monocalcium phosphate is rapidly converted into water insoluble but readily available dicalcium phosphate and, later but slowly, into less soluble tri-calcium phosphate which is not easily available to plants. The products of tricalcium phosphate are liable for further chemical change and may be fixed in soil as unavailable forms of calcium fluorophosphates or calcium carbonate phosphates. However, this process takes place in such a slow rate that in most cases adequate supply to plants would have been complete before the final products of unavailable form result. Calcareous soils do not therefore present such a great problem as acid soils where this process of fixation takes place at a rapid rate.

The reverese process of changing tricalcium phosphate and other compounds into available forms is possible by carbonic acid the supply of which may be increased through decomposition of organic matter. This warrants the necessity of incorporating requisite amounts of organie manure into the soil. This will ensure more phosphoric acid available to plants in such soils where phosphates are fixed by the presence of excess lime in the soil.

Phosphatic fertilisation is problematical in acid soils and those containing hydrated oxides of iron and aluminium which fix the applied phosphates and render them unavailable to plants. Normal applications of super-phosphate say $1\frac{1}{2}$ to 2 cwts. per acre are not therefore effective in such soils and large applications may prove uneconomical. The only possible course left out is to reduce the phosphate fixing power of soil and to make more of the added phosphate available for plant nutrition. Application of phosphate in conjuction with lime to the leguminous crops in rotation, use of silico-phosphates and placement of phosphates near root zone are some of the effective measures. Green manure crops eventually produce organic acids which are absorbed by from and aluminum releasing the fixed phosphates. Lime reduces the pH and influences the release of phosphates. Anantha Krishna Rao and Hanumantha Rao [11] working in the laterite paddy soils of South Kanara in Madras State. have found" a more or less progressive increase in the amounts of available P_2O_5 with increased doses of lime." Varying

doses of superphosphate from 100 to 150 pounds per acre and of lime from 1000 to 2000 pounds per acre were applied. This has resulted in an increase of 10 to 20 percent in yields of paddy. The safe limit of lime application in case of potato crop is perhaps to raise the pH to 6·5 slightly on the acid side of neutrality, because excess liming may lead to fixation again of phosphates by calcium in insoluble forms. Sanyasi Raju and others[12] have experimented the effect of phos-phate on the yield of potatoes and have found that the yield increased with the increase in dose of phosphoric acid in laterite soils of the Nilgiris. It was however concluded that lime itself or in conjuction with P_2O_5 does not influence quality or the yield of potatoes to a great extent.

While studying the phosphate fertilisation in laterite and lateritic soils of Madras State, Venkatachalam and Mariakulandai have found[13] that the availability of phosphate can be doubled by use of silico-phosphate in these soils. It is also reported that about 8 million tons of Trichy phosphate nodules in Madras State are convertible into silico-phosphate which, when made available, may ease the problem of phosphate supply.

PHOSPHATE AND PASTURE LAND

Growth of grasses is stimulated mostly by nitrogen and potash. Still when the pasture does not receive adequate supply of manure, it will utilise the initially existing soil fertility and may quickly show signs of brown top and expose surface soil sooner. Through their premature decay grasses may not respond to application of phosphate unless grown in association with clovers. Grasses produce good yields even when clovers are over sown in pasture land because of the nitrogen fixation which will stimulate the growth of grasses. According to Sears[14] addition of 6 cwts of superphosphate and one ton of lime per acre to pasture land without clover did not increase yields appreciably over those from similar plots without fertilisers. But grassland growing with white and red clovers which were not fertilised, yielded 9000 pounds of dry matter. In such grass and clover combination, the yield was raised to about 12,000 pounds of dry matter, when the land was phosphated. So clovers respond well to phosphate fertilisation and supply increased amounts of nitrogen to grasses growing along with them. It is therefore essential that for proper establishment and high yields of pasture, phosphate should be applied to a grassland having legumes in combination.

In a grass legume association, the application of nitrogen tends to depress the P_2O_5 content of herbage in a soil deficient in phosphates but increases its content in soils rich in phosphates. Yet phosphates is of great importance in animal nutri-tion. It is important to augment its supply particularly in deficient soils. Further while nitrogen will increase the yield of grass, P_2O_5 will enhance the leguminous growth and a proper combination of N2 and P_2O_5 will help maintaining a proper grass-legume ratio which is of significance nutritionally.

CONCLUSION

It is therefore seen that the phosphates play a dynamic role in crop production and in turn in animal nutrition. A large amount of work has already been done on the effect of phosphates in crop production by applying various doses of the phosphatic fertilisers singly or in combination with other fertilisers. However, it will be of great value if more and more attention is paid to the liberation of fixed phosphate in the soil. For this a coordinated study of Soil Types and their pro-perties for evolving suitable methods to release the locked up phosphate so as to make it available to the plant would be very valuable. This would help in ex-

ploiting soil phosphate reserve and indirectly cut down the fertiliser cost, thus making crop production an economic and profitable proposition.

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